

APPENDIX D

University of California Peer Review Comments with Staff Responses

Five experts in the University of California (UC) system were approved by the University of California Office of the President (UCOP) as peer reviewers of the draft ARB report entitled "The Ozone Weekend Effect in California". This report is comprised of two parts – a Technical Support Document (TSD) and a Staff Report (SR) that summarizes the more detailed material contained in the TSD. The reviewers were also provided presentations and reports prepared by other members of the Weekend Effect Working Group. The expert reviewers selected by the UCOP were: Professors Donald Dabdub and Barbara J. Finlayson-Pitts from the Irvine campus, Professor Robert Harley from the Berkeley campus, Professor Suzanne Paulson from the Los Angeles campus, and Professor Gail Tonnesen from the Riverside campus. This group has a diversity of expertise appropriate for assessing the complexities of the ozone weekend effect. Their backgrounds and areas of interest are listed below and include emissions, meteorology, chemistry, ambient measurements, and modeling.

Professor Donald Dabdub -- Modeling of Atmospheric Processes

Qualifications: professor of atmospheric sciences, atmospheric aerosol, and mathematical modeling of air pollution dynamics

Research interests: reactions of sea salt particles to generate photochemically active chlorine and modeling of UV radiation and other factors influencing ozone air quality.

Professor Barbara J. Finlayson-Pitts -- Atmospheric Chemistry

Qualifications: professor of atmospheric chemistry/research chemist, member of the National Research Council Committee on Tropospheric Ozone Formation and Measurement, American Association for the Advancement of Science Fellow

Research interests: reactions of sea salt particles to generate photochemically active halogen gases and reactions of NO_x at aqueous interfaces to generate HONO, HNO₃, and N₂O.

Professor Rob Harley -- Emissions

Qualifications: professor of air quality engineering and air pollution modeling, expert in fuel-based approach to estimating vehicular emissions

Research interests: air pollution sources, atmospheric transport, and photochemical reactions, the role of mobile sources in pollution (particularly differentiating between gasoline & diesel-powered vehicles), role of actinic flux in photochemistry.

Professor Suzanne Paulson -- Hydrocarbon Measurement

Qualifications: professor of atmospheric chemistry courses, expert in hydrocarbon monitoring and chemistry, National Science Foundation CAREER award

Research interests: development of an instrument to better quantify the reactive carbon loading in the troposphere (undetected compounds by current methods may account for more than half of the total reactive carbon), improved understanding of the oxidation chemistry of hydrocarbons (photo-oxidation mechanisms), and improved understanding of alkene-ozone chemistry.

Professor Gail Tonnesen -- Photochemical Modeling

Qualifications: professor of environmental modeling (Eulerian photochemical modeling)

Research interests: numerical modeling of the chemistry and transport of trace gases in the troposphere.

The five peer reviewers submitted a variety of comments ranging from identifying typographical errors, to suggesting editorial and style changes, to making substantive scientific suggestions, to sharing some of their knowledge, insights, and perspectives. The staff of the California Air Resources Board (CARB) is grateful for the time and effort they took in reviewing the material and preparing their comments and suggestions. This appendix includes the complete comments and suggestions made by the UC reviewers interspersed with responses by CARB staff. The peer reviewers' comments are presented in normal type with the CARB response immediately following in a different italicized font.

Although the reviewers came to a variety of conclusions regarding the strength of the evidence for concluding what may be the cause(s) of the ozone weekend effect, they all agreed that changes in NO_x emission are a critical factor. Furthermore, the reviewers noted, whether or not they believed that the NO_x reduction hypothesis explains the weekend effect, that NO_x emission reductions may be needed for a variety of environmental reasons even if NO_x reductions have a slight or temporary negative effect on ozone concentrations. In other words, the varied and variable effects of NO_x emissions ought to be considered before modifications are made in current NO_x control strategies.

The comments are presented in alphabetical order of the reviewers' last name: Dabdub – p. D-3, Finlayson-Pitts – p. D-15, Harley – p. D-41, Paulson – p. D-57, and Tonnesen – p. D-81.

THE OZONE WEEKEND EFFECT IN CALIFORNIA

DRAFT STAFF REPORT

A REVIEW

BY

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THE OZONE WEEKEND EFFECT IN CALIFORNIA TECHNICAL SUPPORT DOCUMENT AND STAFF REPORT

A REVIEW

The ARB staff report and accompanying technical support document entitled “The Ozone Weekend Effect in California” describe the state-of-the-science related to the puzzling phenomenon that is now known as the weekend effect—the observation that ozone measurements in many urban areas are higher on weekends than on weekdays. The ozone weekend effect is surprising to the community of air pollution scientists because smog-forming emissions presumably decrease on weekends. Furthermore, the problem is intriguing not only from the academic viewpoint, but also from the perspective of design and planning of future emission control strategies. In particular, the body of knowledge gained understanding the dynamics of the ozone weekend effect will provide fundamental science required to develop effective policy for emissions control.

Overall the quality of the manuscript is very good. The table below shows specific ratings given by this reviewer. The rest of this document includes specific suggestions and comments that might improve the science, clarify the presentation, or provide additional perspectives to the material presented.

	<u>Poor</u>	Fair	Good	Excellent
Data collection			x	
Data interpretation				x
Sound conclusions				x
Organization			x	
Relevance				x

ABSTRACT

- The abstract should mention that the evaluations of the hypotheses presented involved a combination of field measurements, laboratory studies, as well as mathematical modeling techniques. Furthermore, the abstract can be made more succinct, perhaps to fit on a single page. In particular, paragraphs two and three can be significantly shortened.

Staff made the abstract more germane and succinct. CARB staff did not use modeling to test or evaluate the hypotheses because the current state of modeling has limitations for addressing day of week variations. Models are reasonable tools for evaluating relative differences between potential emission control scenarios for attaining air quality standards but they are not currently adequate for testing fundamental atmospheric processes that we are only beginning to understand. Staff does not believe current models are adequate for truly testing hypotheses of the weekend effect for a number of reasons: 1) emission inventories need to be developed that accurately reflect day-of-week variations in mix, location, and timing of emissions; 2) current model formulations have difficulty generating sufficient O₃ concentrations aloft to match the limited amount of measurements and, furthermore, do not properly handle pollutant movements in the vertical dimension (e.g., pollutant layers are often thinner than model layers); and 3) potentially significant chemical reactions are missing (e.g., low NO_x chemistry in air aloft, halogen chemistry, heterogenous reactions).

EXECUTIVE SUMMARY

- The subsection “Why was this report written?” should be renamed “Why is the ozone weekend effect important?” The first paragraph of the subsection should address that question. The second paragraph of the subsection is less relevant to the Executive Summary and should be removed.

Renamed the subsection “Why is the ozone weekend effect of interest?” as its importance is not known at this time. Deleted the second paragraph as it provides more detail than necessary for the ES.

- The subsection “Are NO_x emissions reductions only relevant to ozone?” should be placed after the subsection “Are NO_x reductions a new feature of California’s ozone control strategies” in order to have a better flow; the NO_x subsections are together and also the two NO_x / VOC sections following are presented together.

Staff agrees that the material in the ES could be organized better and redrafted it.

- The subsection titled “What are the next steps?” lists four thrust areas of future research. The last two thrust areas provide a clear bullet-type summary of the tasks that are planned. However, the “Field studies” thrust area describes the future steps in a more narrative style. It is recommended that this section be presented using the succinct bullet-type style.

Staff articulated more specific objectives to be addressed in future field work.

- The “Laboratory experiments” thrust of the “What are the next steps?” subsection is missing some fundamental science that is discussed in the manuscript. In particular, laboratory studies of the chemical dynamics of NO_x and HNO₃.

Staff included more specific objectives to be addressed in future lab work.

- It would be useful (though perhaps not possible) to indicate the priority and to estimate the costs associated with the main next steps listed in the “What are the next steps?” subsection.

Professor Dabdub makes a good suggestion regarding prioritization of future work efforts. The cost estimates, however, would be quite speculative at this point and probably not appropriate for the ES. Given the tight State budget, only the highest priority weekend effect projects addressing multiple objectives and having co-funding sources have a chance of occurring during the next several years.

INTRODUCTION

- The objectives of the report are clearly stated on page 1-1. However, some objectives do not reflect properly the content of the report. In particular, objective 3 is to identify the causes of the weekend effect. This objective is stated too strongly. As described in the “Executive summary” the report does not demonstrate which hypotheses are correct. It indicates which hypotheses are plausible. Therefore, objective 3 should be changed to something like: to study the feasibility of various hypotheses that may explain a significant portion of the ozone weekend effect.

Staff modified.

- Objective 4 in the introduction is to evaluate the implication of the weekend effect on ozone control strategies. Again, this objective does not reflect the content of the manuscript.

This is a critical objective of the report and the reason behind the Board's directive to

investigate the ozone weekend effect. Staff enhanced the discussion in the report to emphasize its position that the ozone weekend effect, whatever the exact cause(s) of it, has limited and uncertain implications regarding the effects of long-term NO_x emission controls.

- The list of the objectives in the introduction should be highlighted a bit more. A bulleted list might be in order to use here.

Staff believes this subsection is short and succinct and would not benefit from presenting the information in a bulleted format.

- The discussion of the entire document focuses mostly on California. There are a few references and discussions to other locations in the United States. While this is acceptable, the reader explicitly should be made aware that the ozone weekend effect is a phenomenon that has been observed throughout the entire world. Two references that come to mind are:

Switzerland: S. Bronnimann, U. Neu, *Atmos Environ.* **31**, 1127 (1997).

France: V. Pont, J. Fontan, *Atmos Environ.* **35**, 1527 (2001).

Naturally as a state government report, the document focuses on the situation in California and the implications for future research and control efforts in California. That is not to say, however, that the understanding of the California situation cannot be improved by information from other areas where the ozone weekend effect does or does not occur and the potential factors for the different effects. Staff included additional pertinent references of the weekend effect.

- Figure 1.7 on page 1-15 of the Staff Report cannot be read properly. There is no need to show the topography in this graph as it has already been shown in Figure 1-7. The major freeways should be shown on a "white" background.

Staff agrees and incorporated another figure of the highway network in the SoCAB.

- The discussion about the two UCLA studies, while important, does not seem to fit well in the last part of the Introduction.

Staff concurs and has deleted.

- The figures in the Introduction section, as well as all other sections of the Staff Report and the Technical Support Document, tend to be presented at the end of each chapter. The reading experience would be smoother if the figures were included in the middle of the chapters soon after they are discussed in the main

text.

The tables and figures have, for the most part, been included at the end of the chapters as a matter of practicality. As practical in the Staff Report, staff integrated the tables and figures with the text to facilitate smoother reading.

HYPOTHESES OF CAUSES OF THE OZONE WEEKEND EFFECT

The organization of all the hypotheses should contain the following subsections: Synopsis, Theory, Observations, Hypothetical Expectations, and Modeling Insights. Currently, the "Observations" section is more or less included (usually under a different heading). Furthermore, the "Modeling Insights" section is completely missing. This reviewer feels that the contribution from appropriate mathematical modeling exercises should be included in addition to the "Hypothetical Expectations" that can be observed. In brief, the document currently lists specific behavior that can be observed and measured for a given hypothesis. The field measurement tests should be accompanied by computational tests. This is the major weakness of this section and one that will be elaborated on subsequently.

This chapter introduces the hypotheses, the theory behind them, and the expectations in testable parameters. Actual observations of testable parameters are presented in the succeeding Findings chapter. Because of the complexity and overlap of observations with multiple hypotheses, staff deemed its approach of theory, findings, and conclusions to be the most appropriate style of presentation. Staff attempted to relate the observations more directly back to the hypotheses.

Staff has very strong reservations about introducing a "modeling insights" component primarily because the current state of photochemical models is not sufficient for evaluating complex atmospheric processes, potentially contributing to the weekend effect. Day-of-week emission inventories are not available yet for characterizing the complex array of changes from one day to the next. Crude assumptions could be made but the question remains, do the emissions and modeling results accurately represent the real world for the correct reasons? The expense of modeling applications forces models to have limitations in vertically resolving the meteorology and air quality. As mixing depths increase during the day, polluted layers are dispersed into much larger volumes of air than in reality; the pollutants therefore are of much lower concentration and impact when they are subsequently mixed to the ground. Models have historically had difficulty reproducing the proper amount of ozone in the central basin and in the air aloft. Measurements of conditions aloft are very limited (spatially and temporally) and generally confined to episodes with high ozone concentrations. The weekend effect appears to be greater on low and moderate ozone days than on days with high concentrations. How does one apply a limited number of modeling applications to more moderate, but still unhealthy, air quality settings? The chemical mechanisms in photochemical models are constantly being improved. However, there remain a number of processes (e.g., heterogeneous chemistry, halogen chemistry, NO_x chemistry aloft) that remain poorly addressed and likely biased against accurately

characterizing the full effects of NO_x controls. Incorporating the limited number of preliminary (incomplete and based on assumptions about the emissions) modeling applications of the weekend effect into the analysis would create a false confidence in what is known and occurring. Models are based on simplifications of complex atmospheric processes – the modeling results do not therefore define the full extent and interaction of atmospheric processes. There is a place for modeling in evaluating the weekend effect, but the limitations must be known, acknowledged, and addressed. Preliminary and limited results tend to take on a life of their own. Staff preferred not to highlight modeling results until the applications are comprehensive and based on field and laboratory data sufficient to reduce the uncertainties and limitations to minor levels.

- Hypothesis #1: the subsection titled “Emissions in the SoCAB on weekends and weekdays should be renamed “Observations.”

Staff changed the name of the bulleted “Hypothetical Expectations” sections to “Hypothetical Expectations and Related Observations” sections to better portray the major evidence relating to each hypothesis. A new “Limitations” section has also been included to assist the reader in evaluating the evidence.

- Hypothesis #1: The last paragraph of page 2-3 does not belong in the “Theory” subsection. It should be moved to the new “Observations” subsection.

Staff agrees and has moved to the “emission” subsection that follows.

- Hypothesis #1: There should be a new subsection titled “Modeling Insights” that describes some computational experiments that would support or refute hypothesis #1. For example:

If the NO_x-reduction hypothesis contributes substantially to the weekend effect we might expect a computer model to predict higher ozone concentrations when a (hypothetical) Saturday inventory (10-20 percent higher VOC/NO_x ratio) followed by a (hypothetical) Sunday inventory (20-30 percent higher VOC/NO_x ratio) is used instead of when a base case weekday inventory is used.

The above scenario is presented here as an example. It is open for discussion. The main comment being made here is the inclusion of the “Modeling Insight” section to complement the hypothetical observed expectation sections. Insights from modeling exercises can be made immediately without waiting for the perfect weekend and weekday inventories to be developed.

See earlier comments regarding “modeling insights”. Preliminary modeling has been performed by Environ; those results are briefly reported in the “Current/Recent Research”

chapter.

- Hypothesis #2: Typographical error: paragraph 3 on page 2-5 reads “followed by small reductions from 11 p.m. to 3 p.m. produce...” It should read “followed by small reductions from 11 **a.m.** to 3 p.m. produce...”

Staff corrected.

- Hypothesis #2: The subsection titled “Timing of NO_x emissions in the SoCAB on weekends and weekdays” should be renamed “Observations.”
- Hypothesis #2: There should be a new subsection titled “Modeling Insights” that describes some computational experiments that would support or refute hypothesis #2. For example:

If the NO_x-timing hypothesis contributes substantially to the weekend effect we might expect a computer model to predict higher ozone concentrations when a (hypothetical) NO_x-timing emission inventory is used rather than when a base case weekday inventory is used. The total mass of the NO_x-timing inventory should be equal to the base case inventory. However, the (hypothetical) NO_x-timing inventory decreases the amount of NO_x emitted between 6 a.m. and 10 a.m. and increases the amount of NO_x emitted between 11 a.m. and 3 p.m.

Again, the above scenario is presented here as an example. It is open for discussion. The main comment being made here is the inclusion of the “Modeling Insight” section to complement the hypothetical observed expectation sections. Insights from modeling exercises can be made immediately without waiting for the perfect weekend and weekday inventories to be developed. This is repeated here for emphasis. This clarification applies to all the “Modeling Insights” suggestions described subsequently.

- Hypothesis #3: The subsection titled “Emissions and traffic in the SoCAB” should be renamed “Observations”.
- Hypothesis #3: There should be a new subsection titled “Modeling Insights” that describes some computational experiments that would support or refute hypothesis #3. For example:

If the NO_x-timing hypothesis contributes substantially to the weekend effect we might expect a computer model to predict higher ozone concentrations when a (hypothetical) carryover emission inventory is used than when a base case weekday inventory is used. The (hypothetical) carryover inventory is developed with various amounts and types of night freeway traffic.

- Hypothesis #4: The subsection titled “Emissions in the SoCAB on weekdays and weekends” should be renamed “Observations”.
- Hypothesis #4: There should be a new subsection titled “Modeling Insights” that describes some computational experiments that would support or refute hypothesis #4. For example:

Do current simulations show large reservoir of ozone and ozone precursors aloft? Do they mix with the NBL before ozone peaks?

- Hypothesis #5: Some comments related to current emission measurements should be briefly described in a subsection titled “Observations.”
- Hypothesis #5: There should be a new subsection titled “Modeling Insights” that describes some computational experiments that would support or refute hypothesis #5.

Example 1: Increase total mass inventory

If the increased weekend emissions hypothesis contributes substantially to the weekend effect we might expect a computer model to predict higher ozone concentrations when an (hypothetical) increased inventory is used than when a base case weekday inventory is used. The (hypothetical) increased inventory simply adds greater concentration of VOCs and NO_x.

Example 2: Increase reactivity of VOCs

This is the same as Example 1, however the increased inventory contains the same total mass as the base case inventory, while the VOCs of that mass are more reactive than those in the base case inventory.

- Hypothesis #6: Some comments related to current measurements of actinic flux should be described briefly in a subsection titled “Observations.”
- Hypothesis #6: There should be a new subsection titled “Modeling Insights” that describes some computational experiments that would support or refute hypothesis #6. For example:

Current three-dimensional models use as input ultraviolet radiation scaling factors. The photolysis reaction rates are scaled according to measurements made with UV radiometers using correlations such as the ones developed by Zafonte et al (1977). The photolysis reaction rate constants can be predicted independently from estimates of the actinic flux (Peterson, 1976) and from knowledge of the absorption cross-section and quantum yield as a function of wavelength.

If the soot and sunlight hypothesis contributes substantially to the weekend effect we might expect a computer model to predict higher ozone concentrations when the ultraviolet radiation is (hypothetically) increased in the input data.

FINDINGS

- The report contains its results in three different sections. First, some observations summarizing the data are presented after each hypothesis in section 2, "Hypotheses of Causes of the Ozone Weekend Effect." Then, some findings are presented in section 3. Finally, some conclusions are presented in section 4 as well. In order to improve the presentation of results, the findings and conclusions should be consolidated as much as possible into a single section.

This approach may be a little awkward with findings often being consistent with multiple hypotheses. Staff attempted to improve the readability and made the drawing of conclusions more straightforward.

- The findings are presented as isolated observations. Each finding should contain a small paragraph discussing the relevance and role that it might have in relation to the hypotheses being tested as well as the objectives. For example, Finding #2 should be related more directly with objective #2 presented in the introduction. Finding #11 can be easily related with some discussion to Hypothesis #6. In brief, the findings should not be presented in an isolated manner. They should be more integrated with the objectives listed in the Introduction as well as with the hypothesis being tested.

Staff has better integrated the findings and their implications with respect to the hypotheses and the objectives of the report.

CONCLUSIONS

- As in the Findings section, conclusions should be integrated more closely with objectives as much as possible. Some of the conclusions presented (Conclusion #6 in particular) are nicely related to the hypotheses tested.

Staff improved integration of the Findings and Conclusions.

- There is a typographical error on Conclusion #6d, page 4-8. The last line of the second paragraph reads "Repeated from Conclusion 8 above," however there is no Conclusion 8 in the report.

Staff deleted the sentence.

RECOMMENDATIONS

- This section provides an informative summary of the multi-disciplinary effort to follow up the findings presented in the report. It encompasses a balanced effort from field studies, development of emission inventories, modeling studies, and laboratory data. Let me pose the following question: would it be possible to suggest approximate effort (time and funds) to carry out each recommended tasks?

Staff has not provided estimates at this time as they would be speculative.

- Recommendation #4 should include laboratory experiments that provide fundamental insight into the physico-chemical dynamics of NO_x . For example, there is new laboratory evidence that shows that the production of HNO_3 is not the final chemical step of NO_x as we currently believe.

Staff has done.

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REPORT TO CALIFORNIA AIR RESOURCES BOARD

REVIEW OF

"The Ozone Weekend Effect in California"

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June 21, 2002 (revised)

The Task Order requests that a written scientific peer review of the above staff report (SR) and the accompanying technical support document (TSD) be provided. The review "should ensure that the SR is an accurate and clear characterization of the data analyses in the TSD and the scientific literature. Furthermore, the review should ensure that the SR presents sound conclusions, particularly with respect to the potential implications that the Weekend Effect has for the Board's ozone control strategy of reducing both ozone precursors. The reviewer should ensure that reasonable scientific principles were applied in the analysis and in drawing conclusions".

I have reviewed the SR and TSD. Both are very well done and represent a number of different approaches. The staff is to be commended for producing a succinct summary of a very complex issue. I have divided my comments fall into two categories: (1) overall comments, and (2) detailed comments on the SR and TSD.

OVERALL COMMENTS:

The staff report summarizes the data that show a "weekend effect" in some locations and under some conditions, particularly in the South Coast Air Basin (SoCAB) for which the largest amount of data on ozone and its precursors is available. The report presents six possible hypotheses for increased ozone levels on weekends, and on the basis of the data presented in the TSD, rules out two of them (increased emissions on weekends and carryover of pollutants near the ground). Ruling out these two seems to be well-justified by the data in the TSD.

The remaining four hypotheses include reduced NO_x emissions on weekends, changes in the timing of NO_x emissions on weekends, mixing of ozone from aloft, and increased actinic flux and hence enhanced photochemistry on weekends due to reduced emissions of soot. The SR does an excellent job of assessing the available data that are pertinent to these possibilities. What comes through the report is that there continues to be a dearth of data needed to really understand this phenomenon (as well as many other air quality issues). While the NO_x reduction hypothesis is the simplest one to understand and evaluate, the lack of available data to test all of the four plausible possibilities precludes a definitive statement regarding the cause of the "weekend

effect". In this regard, I would not agree with the statement in the **Abstract**, which also appears in other sections of the report, that "The available data provide ample support for NO_x reduction as a factor....". This tends to give a reader much more faith in what is known about the causes than I think the data justify.

Most of the available data from the routine monitoring network vary in manners that are consistent with the NO_x reduction hypothesis, i.e., consistent with VOC/NO_x ratios increasing in a VOC-limited O₃ formation regime. That is not to say the evidence proves the hypothesis but rather supports the hypothesis. On the other hand, much of the available data are not adequate for fully assessing the other hypotheses. This lack of data for testing all the hypotheses does not mean those hypotheses are not correct or don't play a significant role in the ozone weekend effect. Of the hypotheses, the NO_x reduction hypothesis is most easily addressed by the routine data collection. Most of these data are consistent with that hypothesis and therefore the circumstantial evidence is that NO_x reduction must play a significant role in creating the ozone weekend effect. Staff will drop the adjective "ample" from the description of the evidence. Although NO_x reduction may play a major role in the ozone weekend effect, staff is not convinced that it plays a major role with respect to a NO_x control policy. When looking at long-term variations (trends, which are most representative of the impacts of control strategies) rather than short-term variations (WE effect), the greatest improvements in ozone air quality have been associated with periods of greatest reductions in NO_x emissions and concentrations.

There is another potential issue with respect to the soot hypothesis that the CARB staff might wish to consider. Berkowitz et al. [*Atmos. Environ.* **35** 2395 (2001)] reported an anti-correlation between O₃ and particles in an air mass that had passed over Portland, Oregon, and suggested that it could be due to reaction of O₃ with soot particles. The results of subsequent laboratory studies of the reaction of O₃ with soot suggest that this is too slow to be responsible for the observed O₃ losses [Disselkamp et al., *J. Geophys. Res.* **105** 9767 (2000)]; also soon to be published update of JPL Kinetics Summary). However, other studies have observed a similar anti-correlation between soot and ozone in a major city in South America (Prof. Dr. Peter Fabian, personal communication) and in smoke plumes downwind of biomass burning [Tsutsumi et al., *Geophys. Res. Lett.* **26** 595 (1999); Thompson et al. *Science* **291** 2128 (2001)]. In short, decreases in ozone associated with increases in soot particles have been observed in field studies under different conditions and in different locations.

Many physical and chemical processes are at work in the atmosphere and the ambient concentrations reflect the net sum of the effects. As Professor Finlayson-Pitts points out, it is difficult to separate the potential multiple causes from the effects. Aerosol particles, and soot in particular, absorb and scatter UV radiation and the net balance will significantly impact the effects. Furthermore, the particles also provide a surface upon which other physical and chemical changes can occur. Obviously, more fundamental research is needed to definitively address some of these questions regarding impacts.

A major issue with respect to soot reactions is the deactivation of the surface during the reaction; for example, while the reaction of NO_2 with fresh soot generates HONO, surface deactivation as the reaction proceeds makes this source of HONO in air less important than once thought. A possible explanation is found in a recent report by Gutzwiller et al. [*Environ. Sci. Technol.* **36** 677 (2002)] that diesel exhaust generates some as yet unidentified, water-soluble, semi-volatile organics that reduce NO_2 to HONO. It is reasonable to anticipate that if such species can reduce NO_2 , they very likely will also react with O_3 ; however, such compounds would not be present in laboratory studies of soot where conventional methods of generating solid soot particles are used.

Unfortunately, there is little information available that can be used to test this hypothesis at the present time, but it is something that might be kept in mind in evaluating the role of decreased diesel exhaust emissions on weekends on ozone levels, and specifically whether soot and NO_x are the sole issues here. If this were to play a role in urban ozone, it would mean that higher diesel exhaust emissions during the week are reducing ozone; however, increased diesel emissions as a control strategy measure for ozone is clearly inappropriate for a number of reasons, including for example, increased emissions of particles.

Given the significant uncertainties in our understanding of the emissions, chemistry and meteorology, the overarching question is how the current state of affairs should impact California's control strategies for ozone and associated air pollutants, and in particular whether it should alter the emphasis on continuing to control both VOC and NO_x . **My conclusion is that it should not.** The bottom line for this reviewer is that California has had unprecedented success in improving air quality by pursuing this strategy. I recall listening to very similar discussions about 30 years ago when California was embarking on this approach of strict control of both VOC and NO_x . At that time, the argument was made, based on EKMA-type isopleths, that decreasing NO_x would lead to increases in ozone in the most urbanized (upwind) regions of Los Angeles; however, the highest ozone levels in the basin were in the downwind regions. At the time, the isopleths suggested that this might result in a potential trade-off of increased levels of ozone (but on existing lower peak concentrations) in upwind locations in order to improve the much higher ozone levels in downwind locations. What was the result? The SR and TSD show clearly that ozone levels have improved **everywhere** in the basin, including in the upwind locations, despite large increases in population and vehicle miles traveled (Figure 2 of the SR).

Along this line, it is interesting to note an important conclusion from Chapter 1.2 of the TSD that on days conducive to high ozone levels, the data do not clearly establish whether there is a "weekend effect"; ozone peaks on Thursday for these conditions (see Figures 1.2-5 and 1.2-6 of the TSD). The increase from Friday to Saturday for high ozone potential days is given as 0.009 ppm, and Sunday ozone is about the same as on Saturday. If error bars could be put on the 0.009 ppm difference from Friday to Saturday/Sunday, I suspect they would include zero change within two or three

standard deviations. This is a key point for control strategies, where the highest levels are particularly targeted.

Combined with the added benefits of reducing NO_2 , HNO_3 , particulate nitrate and likely other nitrogen-containing compounds such as nitro-polycyclic aromatic hydrocarbons (nitro-PAH), the approach of strict control of both VOC and NO_x has been proven sound and has provided immense benefits to the citizens of California over the past decades.

Staff concurs with Professor Finlayson-Pitts' assessment.

One aspect of this issue that is not discussed in the SR or TSD is that of **long-range** and **global** impacts of anthropogenic emissions. Since NO_2 is the sole known anthropogenic source of ozone, more NO_x over an air basin ultimately leads to more ozone regionally and globally. For example, as seen in the figure below from a classic paper by Volz and Kley, global ozone levels in Europe increased from ~ 10-15 ppb around 1875 to 30 – 40 ppb at even the most remote of continental sites today; Volz and Kley attributed this increased global ozone to increased NO_x emissions from fossil fuel combustion:

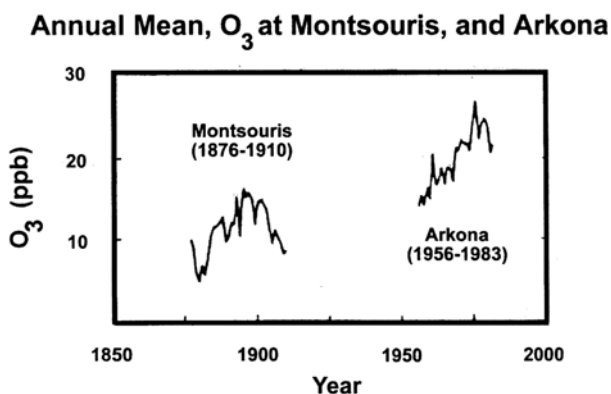


Figure 1.

From Volz and Kley [*Nature*, 332, 240 (1988)]

Similar findings have been reported from sites around the world (see Finlayson-Pitts and Pitts, *Chemistry of the Upper and Lower Atmosphere*, Academic Press (2000) pp. 780-781 for additional references on this subject). Increased levels of ozone on a global basis lead to increased oxidation capacity in the atmosphere, which can impact essentially every reactive trace gas. In addition, such increases have impacts on radiation, since ozone not only absorbs ultraviolet radiation, but is also a greenhouse gas and hence is of concern from the point of view of global climate change.

In short, the regional and global impacts of oxides of nitrogen as they are transported out of urban areas in California provide another very important reason for continuing the highest possible controls on NO_x .

Staff concurs.

The staff report does an excellent job of illustrating what we know and what we don't know. In my opinion, we do not have sufficient understanding of the entire system to justify deviating from what has been a phenomenally successful air pollution control program. What the SR and TSD establish is the very significant gaps in our knowledge and the data bases that need to be filled in order to be in a better position in future years to address these complex issues with a great deal more certainty than is now possible.

There are several issues that arise throughout the report that merit some general comments. The first is the use of VOC/NO_x ratios to interpret the observed changes in ozone, and the second is the geographical extent of the weekend effect. These are discussed in the following sections.

1. Use of the VOC/NO_x Ratio. VOC/NO_x ratios and the associated ozone isopleths (e.g. Figure 2.1 in the SR and Figure 2.3-15 in the TSD) have been used for almost 50 years to predict the impact of VOC and NO_x controls on ozone and other air pollutants. This helps in understanding the chemical reasons for predicted decreases in ozone with increases in NO_x in a static system/box, but it is very important to recognize its limitations:

(a) The isopleth diagram was originally based on smog chamber data and on photochemical box models that were developed to reproduce the smog chamber observations. A static smog chamber or box model is quite different than a real air-basin where transport, complex mixing processes and meteorology, fresh emissions etc. have significant impacts on ozone and other air pollutants. Smog chambers and box models show the effects of changing initial VOC or NO_x concentrations only in an isolated air sample that does not exist in the "real world" where the peak ozone at one location is determined by a complex combination of meteorology, emissions and chemistry, much of which occurs primarily upwind.

As one example (now from the "older" literature, but still illustrative of the principle), Milford et al. [*Envir. Sci. Technol.* 23 1290 (1989)] developed peak ozone isopleths for some selected sites in SoCAB using an airshed, rather than a box, model; the predicted ozone isopleths for upwind locations had a shape similar qualitatively to those of Figure 2.1 of the SR, but the downwind locations such as Riverside/Rubidoux had much more "L" shaped isopleths. That is, the "NO_x quenching" effect was not predicted for the downwind locations where the peak ozone levels were the highest. This is not to say that this particular model result is necessarily correct, but rather that direct extrapolation of the traditional box model ozone EKMA-type isopleths to the complex situation found throughout air basins is fraught with sufficient limitations that direct application to an entire airshed is not appropriate.

(b) These isopleths were developed based primarily on systems that did not include heterogeneous chemistry. Indeed, great efforts have been expended in smog chamber studies to avoid reactions on the walls of the chamber. The “real world”, however, has many different surfaces on which heterogeneous chemistry can occur. Not only are there surfaces in the form of suspended particles, but perhaps more important for the boundary layer, are surfaces of buildings, roads, vegetation etc. The latter have been largely overlooked yet may be very important, especially since most of the available measurements of air pollutants have been made in the boundary layer where these surfaces exceed those of airborne particles; in addition, it is these boundary layer concentrations of pollutants that are used in assessing progress towards meeting air quality standards.

One example of heterogeneous chemistry that must be important in urban airsheds is the heterogeneous hydrolysis of NO_2 on surfaces to form nitrous acid (HONO); the kinetics and mechanism of this reaction are not understood and hence models cannot accurately incorporate it. How important can HONO be? A variety of studies in urban areas in which HONO has been measured show that it is the major source of the reactive hydroxyl radical in the morning, overwhelming such well-known sources as ozone and formaldehyde photolysis. Even when averaged over a 24 hours, it is a major OH source [see for example, studies at Long Beach, CA by Winer and Biermann, *Res. Chem. Int.* 20 423 (1994) and in Milan, Italy, by Alicke et al. and Stutz et al., in press (2002)]. However, known sources of HONO such as direct emissions from cars, or the reaction of NO_2 with the surface of soot particles, cannot account for the measured concentrations of HONO in the atmosphere. It seems likely that the heterogeneous hydrolysis of NO_2 on surfaces is a major source, yet without understanding of the kinetics and mechanisms of this surface reaction, it cannot be included appropriately in airshed models.

Another example is the reaction of gaseous NO with HNO_3 on surfaces to form NO_2 and HONO (“renoxification” of HNO_3) that was recently shown to occur under laboratory conditions by my research group [Mochida and Finlayson-Pitts, *J. Phys. Chem. A* 104 1705 (2000); Saliba et al., *Geophys. Res. Lett.* 27 3229 (2001); Saliba et al., *J. Phys. Chem. A* 105 10339 (2001)]. This, as well as the reactions of other gases such as CO, CH_4 and SO_2 , had been proposed several years ago as being potentially important in the atmosphere by Professor Harold Johnston and coworkers [Fairbrother et al., *J. Phys. Chem. A*, 101, 7350 (1997)]. While the atmospheric importance of the NO-surface HNO_3 reaction is not yet known, the results of preliminary airshed modeling studies [Knipping and Dabdub, submitted for publication (2002)] are intriguing in that inclusion of such a renoxification reaction appears to resolve, at least qualitatively, some long-standing discrepancies between the predictions of airshed models and atmospheric observations of ozone.

For example, the base case airshed model without this chemistry always predicts a single ozone peak in downwind locations of SoCAB such as San Bernardino and Riverside. However, inclusion of “renoxification” of HNO_3 gives rise to model-predicted double ozone peaks in these locations, consistent with most

measurements of the diurnal variation of ozone downwind. In addition, higher ozone levels are predicted at the Central Los Angeles monitoring station when renoxification is included, much closer to the measured values than the base case model; as I understand it from my modeling colleagues, the airshed model historically has underpredicted ozone at this location. Does this mean the NO reaction with surface HNO_3 is important in air? Not necessarily, but what it does strongly suggest is that some heterogeneous chemistry leading to “renoxification” of deposited HNO_3 may be occurring that is not included in current airshed models.

These are just two examples of heterogeneous chemistry that we know about at the present time. It would be naive to think that there are not other such reactions that may have a significant impact on model predictions *if* their chemistry were recognized and understood in sufficient detail to include them in such models.

(c) Even *if* the limitations of using VOC/ NO_x ratios to develop control strategies discussed in (a) and (b) did not exist (but they do!), accurate measurements of VOC and NO_x are needed. The TSD and the SR do an excellent job of assessing the current status of such measurements. In brief, as described in the TSD in Chapter 2.1.4.5, “continuous measurements of THC are only available for a handful of sites and even those discontinued monitoring in 1995”. Chapter 2.3 of the TSD discusses the PAMS (“Photochemical Assessment Monitoring Stations”) data for VOC and points out that these data may underestimate the total hydrocarbon concentrations by about 30%. In addition, the assessment used to estimate VOC/ NO_x ratios did not include carbonyl compounds, which are some of the most reactive organics found in air.

The NO_x data also have significant limitations that are pointed out in Chapter 2.1 of the TSD. First, what is really measured is NO_y (i.e. the sum of all nitrogen-containing compounds that can be reduced over the instrument catalyst to NO) and not $\text{NO}_x = \text{NO} + \text{NO}_2$. In relatively unreacted air masses, NO_y is generally in the form of NO and NO_2 (i.e., NO_x); however, in aged air masses, there is often a large discrepancy between NO_x and NO_y , and also between the sum of measured individual nitrogen compounds and the total measured NO_y . The figure below, for example, shows some measurements made in Colorado in air masses with different ages.

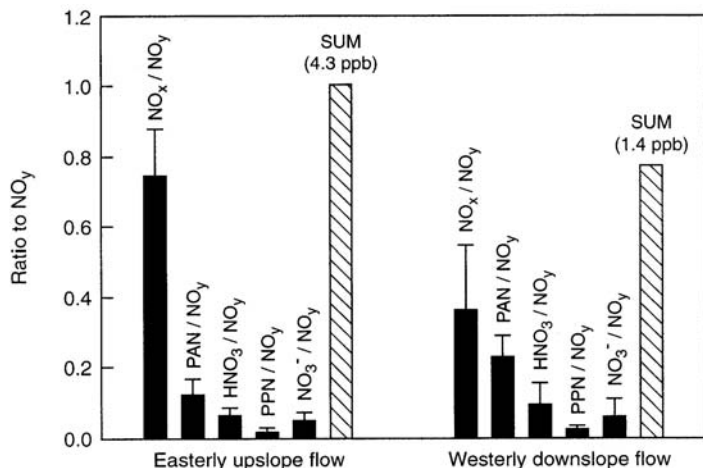


Figure 2. Ratio of measured individual compounds to total NO_y at Idaho Hill, Colorado, with easterly winds (more polluted but less aged air) compared to westerly winds (less polluted but more aged air). Data from Williams et al, *J. Geophys. Res.* **102** 6297 (1997).

In the less aged air mass, NO_x was 75% of NO_y , while in the more aged air mass, it accounted for less than 40% of NO_y . This illustrates that particularly in downwind regions in California air basins, the “ NO_2 ” and hence NO_2/NO ratios may be significantly overestimated.

The TSD points out that even the NO measurements have significant uncertainties, particularly in the afternoon because they approach the instrumental detection limit (e.g. Chapter 2.1.4.4 of the TSD).

Of course, the uncertainty in the ratio of VOC to NO_x will be larger than the uncertainty in either one. Thus, while the staff have done a very good job of trying to estimate this ratio under various conditions, it must be recognized that the lack of accurate, long-term data for both VOC and NO_x significantly hampers using this metric to elucidate the association between the VOC/ NO_x ratio and air quality.

Professor Finlayson-Pitts has done an eloquent job of articulating the uncertainties and unknowns regarding the measurements of VOCs and NO_x . While the VOC/ NO_x ratio is a crude tool for assessing O_3 formation, it is the best readily available indicator of ozone formation dynamics. This serves as an example of the frailty of using the available evidence without understanding the underlying limitations. Whether ratios, modeling, emission inventories, etc., a superficial look at the evidence without a thorough understanding of the limitations can lead to the conclusion that the evidence is definitive rather than circumstantial.

2. Geographical Extent of the “Weekend Effect”. It is interesting that the “weekend effect” is observed in two air basins that are coastal, Los Angeles and San Francisco, but apparently either does not occur or is not as evident in the San Joaquin Valley and the Sacramento area. There are several potential differences between the coastal air basins and those inland.

First, the coastal air basins are affected by the land breeze-sea breeze phenomenon, so that there is presumably some “sloshing back and forth” of air masses. Second, there is the possibility that chemistry unique to coastal regions plays a role. For example, sea salt is a source of chlorine atoms that reacts rapidly with organics, initiating the VOC- NO_x chemistry faster than would otherwise be the case; at low organic concentrations, chlorine atoms react preferentially with O_3 [for example, see De Haan et al, *Int. Rev. Phys. Chem.* **18** 343 (1999), and Finlayson-Pitts and Pitts, *Science* **276** 1045 (1997); Andreae and Crutzen, *Science* **276** 1052 (1997); Ravishankara, *Science* **276** 1058 (1997)] Sea salt particles are also a source of bromine atoms that are known to carry out a chain destruction of ozone in the Arctic at polar sunrise ([e.g. see Foster et al., *Science*, **291** 471 (2001)] but that also have been proposed to play a role in ozone

chemistry in mid-latitudes [e.g. see Dickerson et al., *J. Geophys. Res.* 104 21385 (1999); Nagao et al., *Geophys. Res. Lett.* 26 3377 (1999)].

Another potential difference in inland versus coastal areas that may affect the chemistry is the concentration of ozone and its precursors upwind. Ozone levels over the remote Pacific Ocean at the surface appear to be in the 10 –15 ppb range [e.g. see Oltmans et al., *J. Geophys. Res.* 106 32503 (2001)], lower than continental values of 30 – 40 ppb. However, data provided by the ARB staff on measurements at San Clemente Island in the mid-1990's show July – September levels of ~ 35 – 40 ppb, similar to the continental “remote” values. It is not clear to me whether this reflects an effect of emissions from the SoCAB (perhaps including those associated with port or offshore military activities) on ozone levels at San Clemente Island, which are then carried to the coast during the day or whether there is some reason that the “clean” air at San Clemente Island has higher ozone levels than the Pacific Ocean to the west of it.

Professor Finlayson-Pitts raises some interesting geographic differences (complex air flow patterns, above typical upwind “background” O₃ concentrations, and sea salt chemistry in coastal regions) here that could be investigated further. However, the areas where the ozone weekend effect is observed does appear to be increasing in size over time in the coastal air basins; furthermore, it is now also becoming evident in the major urban areas of the Central Valley.

DETAILED COMMENTS ON SR AND TSD

The remainder of this report includes specific comments on the SR and TSD. Overall, the staff has done a remarkable job of bringing together a variety of data. Many of the comments in the following are examples of the issues discussed above, or are editorial in nature; they are offered to improve the utility of the report for non-experts for whom this report will be of great interest and value.

STAFF REPORT:

Abstract:

The first sentence of the third paragraph on page vii states that the strategy of reducing both VOC and NO_x has been “highly successful at reducing ozone levels on all days of the week in areas where the ozone weekend effect is the strongest”. It seems to me that the data show it has been highly successful everywhere, not just where the weekend effect is the strongest. In fact, if anything, the data seem to me to show the weekend effect is less obvious in downwind locations in SoCAB such as Riverside-Rubidoux where ozone reductions have been quite dramatic over the past 20 years.

Staff has clarified sentence (i.e., “areas”) to indicate focus of statement being coastal metropolitan air basins versus interior air basins rather than different sub-regions of the SoCAB.

Executive Summary.

Page xii. “Does the ozone effect occur everywhere?”. It is not obvious to me that “The ozone effect presently occurs at most, if not all, of the monitoring sites in the Los Angeles....”. If the 1998 data for Riverside, for example, were omitted, it would be difficult to argue from a visual examination of Figure 3 that there is a weekend effect here; the weekday and weekend data seem to intertwine and cross on a frequent basis. This section of the SR is based in part on Figures 1.1-1 to 1.1-18 of the TSD that show the trends in the mean of the 2nd to 11th highest daily 1-hour ozone values from 1980 to 1998, separated as weekday and weekend averages, for a number of monitoring stations in SoCAB; for most locations shown in these figures, the general trend appears to the “naked eye” to be a faster decline in ozone for weekdays compared to weekends. Having error bars (2σ) on the points would help the reader assess the precision of the data in these plots. For example, most plots seem to show an upward “spike” in the last year of data shown, particularly for the weekend values; if this last point were omitted in the Riverside-Rubidoux data for example, (Figure 1.1-12), a “weekend effect” at that location would not be obvious, at least to this reviewer.

Including uncertainty bars would clutter the general message being presented. A 2σ uncertainty bar characterizing intra-annual variability would be about 0.020 ppm and reduce much of the difference between WD and WE at some sites. The weekend effect is relatively small but it is real and the area where it occurs is increasing. With regard to the 1998 data point possibly giving a false impression, the plots in Chapter 1.2 of the TSD suggest that it is the WE 1997 average that is atypically low (strong El Niño year).

The statement at the bottom of this page, “...the ozone weekend effect tends to be smallest at those sites that measure the highest ozone concentrations” is very important and should be highlighted. For example, Figures 1.2-5 and 1.2-6 from the TSD might be good additions to this section to illustrate this.

Staff has increased emphasis by adding a figure of exceedances of the 1-hour California standard at a cross-section of sites in the SoCAB. However, the additional technicality provided by the figures in the TSD are not appropriate for the Executive Summary. The general impression provided by the Riverside (peak ozone region) and Azusa (central basin) plots in Figure 3 already supports this statement. The contrast of the weekend effect with exceedances spatially and historically in Figure 2 will emphasize the point further.

Page xiv, “Do other air pollutants exhibit a weekend effect?” There is reference here to NO₂ concentrations. However, what is measured is actually NO_y, which for downwind locations especially may be quite different (see Figure 2 above). Although this is in the “Executive Summary” and hence abbreviated, some mention of this here would be appropriate to illustrate the uncertainties in the available data.

Professor Finlayson-Pitts is correct in noting that NO_2 measurements include additional oxidized nitrogen species, such as PAN, volatile nitrates, and some nitric acid, and that this "contamination" would be greater in the downwind regions; however, NO_2 measurements are also not NO_x as many of the more oxidized nitrogen species tend to stick to the sampling line and are not measured. Staff has included a parenthetical note.

Page xiv: The last paragraph states that "...VOC/ NO_x ratios at ground level are less than 8 to 10 in most of SoCAB". Given the uncertainties in, and in some cases lack of, data on VOC and NO_x (true NO_x , not NO_y), it seems to me that this implies a greater certainty in our knowledge of this ratio than the data in the TSD can support. See also earlier comments on VOC/ NO_x ratios. Same comment on page xvii after the statement "The NO_x -reduction hypothesis is plausible".

The measured VOC/ NO_x ratios (at ground level) in the SoCAB are quite low. Even with a 40% increase in the ratio due to negative biases in the VOC measurement and positive biases in the NO_x measurement, weekday ratios tend to be below the peak ozone production efficiency ratios of 8 to 10. Weekend ratios tend to be sufficiently higher than the weekday ratios that they tend to be in the more efficient O_3 production range. That said, the important question is the usefulness of VOC/ NO_x ratios as an O_3 formation indicator. The ratio varies spatially and more so temporally. Midday measurements are likely to be biased low even more so than the morning measurements. Also, this indicator is based on surface measurements near sources. The most important question is "how representative are these spatially and temporally limited measurements of conditions where the bulk of the O_3 production is occurring, away from fresh emissions (i.e., the central block instead of the traffic corridor or tens to hundreds of meters above the ground)? This is a fundamental research question that we hope to address within the next few years, assuming funding is available.

Page xix: "The soot and sunlight hypothesis is plausible theoretically". It is not clear to me why the word "theoretically" is included here and not for the other three hypotheses. If its meant to imply that there are fewer data to try to evaluate this, this should be so stated and "theoretically" removed. As discussed earlier, it may be that there are also chemical reactions associated with the emissions of soot and associated semi-volatile organics that lead to ozone destruction. While there are too few data to address this in detail, perhaps a line or two should be added that recognizes that there may be other effects than just that on light intensity.

Staff has done.

Page xx: "Laboratory Experiments". The greatest source of uncertainty is heterogeneous chemistry, which is not mentioned here, but should be. The statement that "Present generation smog chambers reduce experimental artifacts compared to earlier chambers" is actually quite interesting, since these "artifacts" usually involve wall reactions. Because they are not understood, the approach has been to try to minimize

them. However, certainly such reactions must occur in ambient air as well. As discussed earlier, reactions on roads, buildings, vegetation etc. in the boundary layer have been virtually ignored, but have the potential to play a very significant role in this lowest region of the atmosphere where the emissions are occurring and the vast majority of measurements are made.

Staff has done.

1. Introduction and Background.

Page 1-2. The statement is made that “Without VOCs and NO_x from human activities, ozone concentrations near the earth’s surface would be limited to approximately 20 to 40 ppb”. I believe the correct range for continental ozone is more like 10 –15 ppb, which was observed before the industrial revolution (see Figure 1 above and references in the Finlayson-Pitts and Pitts book, pp. 780-781. Over the remote Pacific, current ozone levels of 10 – 15 ppb have also been observed [e.g. see Oltmans et al., *J. Geophys. Res.* **106** 32503 (2001)], which likely reflects more rapid destruction of ozone at the surface than the rate it is being replenished from the air aloft that has higher ozone. Also, isn’t O₂ about 21% of the earth’s atmosphere, not 18%?

Staff has corrected.

Page 1-5. Third paragraph. “Assuming meteorology is unaffected by the day of the week,...” A naive question from a chemist: is this assumption valid? I am wondering if the turbulent mixing caused by the motion of cars on freeways, as well as the heating effects from the cars, might affect mixing close to the earth’s surface where most measurements of air pollutants are made?

Undoubtedly, there are micro-scale and urban-scale anthropogenic effects on the meteorology (temperature in particular). The day-of-week differences appear to be quite small, if in fact they are real (Blier et al., 1996). Meteorological variation is the largest determinant in air quality in urban areas (emissions may be identical but the air quality could be very different). Thus, the air quality impact could be significant compared to the small meteorological deviation. Unfortunately, the uncertainty (“noise”) in the meteorological measurements precludes a definitive assessment of this assumption of meteorology being unaffected by the day of the week.

Page 1-7. The meaning of the first “bullet” is not clear to me. That is, the reason why maximum ozone in a particular sub-region should “relate more strongly to morning NO_x concentrations locally than to NO_x concentrations in any other sub-region” is not clear, since transport is well known to be important. Perhaps some comment on why the authors of the report think this is the case could be included, or a caveat added.

This finding does not dispute the impact of transport but rather emphasizes that local O_3 air quality varies in association with the local NO_x emissions, i.e., that local NO_x is the “kicker” in determining the absolute O_3 peak. Although the association is with morning NO_x , the real cause and effect may be local NO_x activity because the NO_x emissions react so fast in the afternoon that NO_x concentrations are very low and the “signal” is lost in the “noise” of the data. Furthermore, this finding indicates that O_3 quenching is a temporary effect.

Also, there are references throughout to reports by Blier and Winer, but since there are more than two authors, should it not be Blier, Winer et al.?

Staff corrected and has also changed references to “Blier et al.”

2. Hypotheses of Causes of the Ozone Weekend Effect.

Page 2-1. Second paragraph. I would suggest adding “...destruction and transport..” after “ozone formation” to read “It is difficult because ozone formation, **destruction and transport** in the lower atmosphere....”

Staff inserted “and destruction or transport”.

Page 2-3 to 2-5. It might be useful here to reiterate some of the statements made in other parts of the report about the need to consider the entire air basin in context and the limitations of applying VOC/ NO_x ratios. As discussed above, the uncertainty in the VOC and NO_x measurements is not conveyed in the paragraph on the bottom of page 2-3; when VOC is uncertain by ~ 30% or possibly more, and measurements are made of NO_y , as a surrogate for NO_x , and with NO sometimes being around the instrumental detection limit, changes of 10 – 30% cited seem to imply more certainty in these measurements than there appears to be.

Staff has included a caveat regarding the accuracy and use of the ratio.

Page 2-5. Figure 2-4 appears out of order.

Staff has corrected the numbers and the order of reference to the figures.

Pages 2-9 and 2-10. It is not clear to me why the air mass aloft should be NO_x limited. Air masses aloft are isolated from surfaces on which deposition of nitric acid and other NO_y can occur and hence may be longer-lived than in the boundary layer. The analogy that the “air aloft has traveled “downwind” vertically rather than horizontally...” is not obvious to me. There have been some recent studies in Houston and Phoenix that did

some surface and altitude measurements that may shed some light on this. For example, Dr. Jochen Stutz (UCLA) has carried out DOAS measurements of various gases from the top of a building in Phoenix, with the light beam directed at three different angles in order to probe vertical profiles. By arbitrarily breaking the vertical section into three layers, he and his coworkers were able to show greatly enhanced NO_3 and HONO, for example, in the top layer [e.g. see Berkowitz et al., abstract in *Am. Meteorol. Soc. Meeting* (2002)].

Staff's statements are based on the shorter atmospheric lifetime of NO emissions compared to VOC emissions and from aircraft spiral data that indicate the NO and NO_2 concentrations decline rapidly with altitude. That is not to say that other reaction products don't increase (in fact, by conservation of N, they must). Undoubtedly, NO reactions are occurring rapidly outside the surface layer where fresh NO emissions are continuously being injected. Important photochemical reactions are occurring above the monitoring network and this causes staff to wonder: 1) based on lidar and aircraft data, is the large air mass above the immediate surface layer where most of the O_3 observed at the surface monitors is produced? and 2) are NO emissions late in the day being sequestered aloft (e.g., HONO) and available for "kicking off" O_3 formation at sunrise the next day? The ambient data suggest that carryover of the extra Friday and Saturday night emissions does not occur in the surface layer but little is known about the impact of those emissions that might be mixed aloft in the evening and sequestered from surface deposition and destruction. Staff hopes additional work will be funded in the next few years to better document the chemistry occurring above the immediate surface layer to which our routine measurements are limited.

Page 2-12. In the "hypothetical expectation" that "comparisons of weekday-specific and weekend-specific emissions inventories should (hypothetically) identify increased emissions"..., the emphasis should be on "hypothetical". Given the historical underestimation of emissions, it is not clear to me that the current state of emissions inventories would be sufficiently accurate to make a meaningful comparison.

Staff concurs that the uncertainties in generating emission inventories would probably preclude identifying such a difference with any certainty.

Page 2-12. In addition to soot, there are some data [e.g. Malm et al., *J. Geophys. Res.* **101** 19251 (1996)] that suggest that there are unrecognized organics that also lead to light absorption. This would not be surprising, given that oxidized organics are likely to contain carbonyl groups which absorb light in the actinic region.

Staff has added "organics".

3. Findings.

Page 3.1. Some comment might want to be made regarding the fact that both air basins showing the “weekend effect” are coastal.

The facts that the spatial extent of the weekend effect spread eastward in the SoCAB and the beginning of the effect in major urban areas of the Central Valley suggest that urbanization is a greater factor than the coastal setting. However, the complexity of air flow in a coastal setting may well exacerbate the weekend effect in the coastal areas.

Page 3-3. It is not clear to me what is being compared to what in Table 3.3. Are these peak O₃ values? Averaged over what? What does “1980/82 baseline values” in the first footnote mean? Similarly, the definition of the “Difference” shown in the table as described in the second footnote is not at all clear to me.

The net change in ozone air quality from the early 1980s to the mid-1990s is compared for weekdays and weekends. During this period, O₃ levels in the various portions of the SoCAB declined 42-55 percent on weekdays and 26-43 percent on weekends; i.e., O₃ declined faster on average on weekdays than weekends. The difference in the percent improvement on weekdays versus on weekends is expressed as “points”; e.g., the average decrease on weekdays was 46% while the average decrease on weekends was 33%, resulting in a preferential decrease on weekdays of 13 percentage points. The trending statistic is the annual mean of the 2nd-11th highest daily maximum 1-hour O₃ concentrations. This trending statistic is now identified in the footnote.

Page 3-4. Error bars (2σ) on the 9 ppb and the 29 ppb numbers would help the reader assess the uncertainty in these.

The author did not provide uncertainty estimates for these statistics but likely to be about 10-15 ppb.

Page 3-7. Finding #11. The three statements included here to me imply much more certainty regarding our knowledge of VOC, NO_x, their ratio and that of NO₂/NO than justified by the data in the TSD. In fact, near the top of the page it is stated that “A similar analysis based on direct measurements of VOC’s was not possible due to limited data”.

Staff’s revision to the report noted the uncertainties in the measurements and stated that the data “indicate” rather than “show”.

Page 3-8. Finding #12. Same problem as for Finding #11.

Staff condensed and reorganized these findings as they overlap and appear redundant.

Pages 3-10 to 3-12. The TSD mentions that the traffic counts are based on freeway counts, not surface streets. It seems to me that this is an important point that should be mentioned here.

Staff has noted the limited scope and uncertain representativeness of the freeway data for activity on surface streets.

4. Conclusions

#1. I would again include some comment about it being observed in the two coastal air basins, even if the reason for this is not currently understood.

Staff chooses not to include an uncertain association in the Conclusions section.

#2. The last statement in the conclusion that the weekend effect occurs throughout the SoCAB is not necessarily the case, it appears to me, since the data for downwind locations like Riverside and Lake Gregory up to 1998 seem not to consistently show this effect.

Although the weekend effect is recent and relatively small at the downwind sites in the eastern portion of the air basin, staff believes adequate evidence is presented in Chapter 1.1 of the TSD to support this conclusion.

#3. Agreed. May want to add something regarding regional and global impacts as discussed above.

Staff has done.

#6a. At risk of sounding like a “broken record” (or I suppose a broken CD nowadays), I am skeptical about the three statements made in the bullets here. Same for first two bullets in **#6b**.

Staff has caveated.

#6f. As discussed earlier, remove “theoretically”.

Staff removed in heading but included in text.

5. Recommendations.

#2. I recommend including surface street traffic in this.

Staff has specifically noted the need for surface street activity data to supplement the freeway data being collected.

#3. In the modeling studies, I recommend including some studies that address what are apparently traditional discrepancies between the model predictions and observations. For example, it is my understanding (but I am certainly willing to be corrected by my modeling colleagues) that airshed models do not predict the double ozone peaks commonly observed in downwind locations and underpredict ozone at Central Los Angeles. In addition, while average 24 hour nitrate is reasonably well predicted, the diurnal variation at least in some locations is not. Such discrepancies suggest there is some chemistry and/or meteorology that is not being accurately represented, which then raises a question regarding relying **primarily or solely** on such models to assess the causes of the weekend effect and the associated implications for controls of VOC versus NO_x.

Staff concurs and has included in the revision of the report.

#4. A major focus of laboratory studies should be on heterogeneous chemistry. Because of the great difficulty in carrying out meaningful studies in this area which would provide the molecular level understanding needed for accurate representation in airshed models, there is very little known. However, the potential for an impact on the model predictions (and of course, the real-world chemistry, which is what matters) is sufficiently great that concerted efforts should be directed to this area.

Staff concurs and has included in the revision of the report.

TECHNICAL SUPPORT DOCUMENT:

Chapter 1:

Figures 1.1- to 1.1-18 and Tables 1.1-1 and 1.1-2: Giving 2 σ error bars on some of the points (e.g. around both ends of the data and the middle) would help the reader to appreciate the uncertainties in the trends/data. (This may be beyond the scope of this analysis, however).

Staff did not incorporate the uncertainty estimates in tables and figures but will pursue a general estimate.

Table 1.2-1: Putting a footnote in the Table describing what “high”, “low” and “medium” mean would help the reader.

Staff has done.

Table 1.3-2: What is the asterisk for in the title? ("change*") Error estimates of the data in the table would again help, e.g. are three significant figures as given for some entries meaningful?

Staff deleted the asterisk and round the day-of-week change to the nearest percent.

Chapter 2:

Page 2.1-5 (Section 2.1.4.3): Are there any data available that might indicate how much of the "NO_x" is really "NO_y"?

The available data suggest that the two measurements are very similar with some spatial (depending on the proximity and strength of local sources) and diurnal variations (depending on the chemical and photolytic reactions occurring). That does not necessarily mean the NO_x analyzer is recording a lot of NO₃, PAN, PPN, and HNO₃ but rather that surface-based measurements are dominated by fresh NO emissions and NO₂ formation. Although PPN and HNO₃ in particular would have difficulty reaching the reaction chamber because they would tend to "stick" to the sampling line, the relative amount of these materials are small and the NO_x concentrations tend to be the same or slightly ($\leq 10\%$) less than the NO_y concentrations.

Page 2.1-8 (Section 2.1.4.4.2): Could another reason for the higher NO₂/NO, particularly in the early evening, be that what is really measured is NO_y? One might expect a larger contribution from other nitrogenous compounds in aged air masses, i.e. later in the day and at downwind locations.

Professor Finlayson-Pitts makes a good point regarding the evening NO₂ measurement probably also including higher oxidized nitrogen compounds than the morning measurements. However, that would not necessarily explain the transition from 1994 to 1998 to a higher evening peak than morning peak for NO₂/NO ratios unless the NO_x emissions were declining faster than the VOC emissions and the NO oxidation cycle was sped up by the relative excess of VOC radicals.

Page 2.1-9 (Section 2.1.4.5.1): It is stated that THC concentrations are lower in the summer than in winter. Perhaps I missed it, but I did not see data supporting this statement. It seems surprising that this would be the case, since one might expect with the higher sunlight intensity and temperatures during the summer, the contribution of biogenic organics would increase.

It is true that biogenics and evaporative VOC emissions are greater during the summer than the winter. But the great determining factor in ambient concentrations is meteorological dispersion, particularly in the vertical dimension. During the winter, strong radiative cooling can create surface-based inversions that trap the fresh emissions at ground level. During the summer, the

inversions are not as frequent, strong, or persistent and the surface concentrations of pollutants are lower than on winter days without precipitation.

Second paragraph from the bottom (Section 2.1.4.5.2): "At mid-day, the NO_x concentrations..." Shouldn't "NO_x" be "THC" here?

Professor Finlayson-Pitts is correct and staff has corrected in final report.

Page 2.2-1: "VOC" is used here, but THC in previous sections. It is not clear to me whether there is a distinction between the two terms or they are being used interchangeably.

"THC" was used in the previous chapter because it refers to the Total HydroCarbon measurements made with a continuous analyzer and therefore useful for providing some insights into diurnal dynamics. This measurement includes methane (CH₄), which has significant natural and anthropogenic sources and also frequently comprises more than half of the THC measurement. "VOCs" are included (though under-reported) in the THC measurement. VOCs are much more reactive than CH₄ and therefore of greater interest in O₃ formation discussions.

Page 2.2-3: Is the last sentence saying that the "weekend effect... now encompasses the entire SoCAB" correct? As per earlier comments, the data for downwind locations are not convincing, and in addition, it is not clear that the effect exists on the "high ozone conducive" days.

Staff are quite confident that the WE effect can be found throughout the SoCAB, albeit much weaker on high O₃ days and at some sites.

Figures 2.2-87 and -88: These figures are not clear to me; what do the different bars represent?

Staff has clarified. Each plot has 3 groups of 6 bars. The first group (#1) represents data for Los Angeles; the second group (#2) represents data for Azusa, and the third group (#3) represents data for Riverside). Each pair of six bars represents a different year – first pair - 1982, second pair - 1988, and the third pair - 1995. The first bar in each pair represents data for Saturday compared to weekdays and the second bar represents data for Sunday compared to weekdays. Note in Fig. 2.2-88 that Sunday became the peak O₃ day at Los Angeles in 1995, at Azusa in 1988, and was already the peak day at Riverside in 1982.

Table 2.3.3: The very low VOC/NO_x values for Banning do not seem intuitively correct to me. If the usual argument is made that this ratio is typically larger in downwind locations, values around 2-5 in the morning seem very low. I suspect this reflects the uncertainty in both VOC and NO_x, since NO_x levels are low and many of the organics may be in the form of oxidized species that are notoriously difficult to sample and measure accurately. Given this, citing VOC/NO_x ratios to three significant figures in this and similar tables seems to be somewhat optimistic; probably one significant figure is what might be known, at best.

The data shown in Table 2.3-3 are misleading due to the undue impact of local sources. The local district is investigating and likely to invalidate the data. This Table has been dropped from the report. Staff has reduced the data in the remaining tables to 1 decimal point for presentation purposes.

Figure 2.4-1 and –2: The bars in these figures were indistinguishable, at least in the copy that I had for review.

Staff revised the color scheme to allow better reproduction of the data bars in black and white.

Chapter 3:

Page 3.1-1: There are two different figures marked 3.1-1, one in the text and a different one at the end of the chapter.

Staff has corrected.

Page 3.1-2: Addition of some of the key references to health effects in the last paragraph would be helpful to many readers.

Staff has done.

Page 3.1-3: A major source of nitric acid formation at night is the NO_3 radical and N_2O_5 hydrolysis on surfaces. These should be included in this discussion, with some mention of the importance of deposition of HNO_3 as a major loss process. Also, the Finlayson-Pitts and Pitts reference is 2000, not 1999.

Staff has done.

Pages 3.1-9 and 3.1-10 (Section 3.1.5.1): The statement is made that “The day-of-week differences in trend have no obvious explanation and raise questions about adequacy of the available data”. I agree with this, but it might be helpful to make such a statement at the beginning of this section.

Staff has elaborated and noted in the first paragraph under Methodology.

Table 3.1-1: Why not show the exceedances for all four air basins for both the federal and state standards?

Staff has done.

Table 3.1-2: Given the potential artifacts in measuring nitrate discussed in the text, perhaps the data should be reported to 2 sig figs at most?

Staff rounded to nearest $\mu\text{g}/\text{m}^3$.

Table 3.1-3: Without error bars, it is difficult to assess what changes are meaningful. Again, this may be beyond the scope of this report but if so, the addition of a caveat would hopefully prevent a reader from assigning more certainty to some of the changes that can be justified.

Uncertainty estimates were not provided but will be asked for in future analyses.

Chapter 5:

Page 5.1-1: It would help the reader to briefly restate the hypotheses in the bottom paragraph, rather than referring to them by number only.

Staff has done.

Table 5.1-3: It would help to replace the day of the week numbers with the day itself.

Staff has done.

A particularly important aspect of this chapter seems to me to be that the data reflect freeway counts only and not surface street traffic. This could be especially important in that the amount of surface street traffic relative to freeway traffic could be quite different weekends compared to weekdays. Presumably, the driving cycle and associated emissions on surface streets are also different than on freeways, which could impact emissions.

Staff agrees and CARB has contracted for a limited assessment of the difference between traffic activity at a WIM freeway site and on a nearby surface street. Preliminary results indicate that they are highly correlated but that might be expected if the surface street traffic count is made near an access point to the freeway. Additional work is warranted in areas that are a few miles from the freeway to better capture weekend trips to local stores, parks, service stations, etc.

Page 5.3-1: What is the reference for the "...recent emissions inventory..." in the 2nd paragraph?

Staff provided the reference.

Figure 5.3-3: What does "Pseudo VOC/NO_x..." mean?

Staff has defined and corrected the text to match the figure content.

Chapter 6:

An impression I have from the literature is that ironically, ozone is one of the easiest pollutants to model in terms of matching the field observations. If one goes back into the literature in the 1980s, one can find some good matches of the models to the measurements of ozone in the South Coast air basin. However, we know now that the mobile source emission inventories for VOC and CO were underestimated by factors of 2-4 at that time. The fact that good matches could be obtained suggests that ozone is not a very sensitive test of how accurately models represent the true atmospheric processes. A number of papers [e.g., Dodge, *J. Geophys. Res.* **94** 5121 (1989); *J. Geophys. Res.* **95** 3635 (1990)] have shown that other species such as H₂O₂ and HCHO are less “forgiving”. The reason this is important is that if one gets the “right answer but for the wrong reasons” in terms of predicted ozone, then relying solely on models to predict the effects of different control strategies is risky in terms of the uncertainties in the predictions. It might be appropriate in this chapter to point this out as well.

Staff has raised this excellent point in the introduction to modeling concerns.

Page 6.1-2: First sentence of the “Introduction” seems to imply that the NO_x reduction hypothesis is the cause of the “weekend effect”. As per the comments above, I am not convinced that this is the only/major cause.

Staff redrafted to avoid the potential implication.

Page 6.1-5: The reference on line 9 should be Knipping et al. (2000), not Dabdub. The reference on line 11 should be Finlayson-Pitts and Mochida (2000) (not just Finlayson-Pitts) and the following reference should be added after the Finlayson-Pitts and Mochida: N. Saliba, M. Mochida and B. J. Finlayson-Pitts, *Geophys. Res. Lett.* **27**, 3229 (2000).

Staff has done.

Page 6.1-7 and 6.1-10: You might want to reference the Phoenix study in terms of concentrations of species aloft and vertical mixing (see discussion of work by Stutz et al. above); these data should help to understand these issues much better.

Staff mentioned.

Appendix C:

Pages C-3 and C-4: 1a), line 7: “Although staff suspects that the NO_x reduction is a major factor in the Ozone Weekend Effect...” seems to contradict the rest of the TSD and SR that while it may be a factor, there are other potential causes/contributing factors that cannot be ruled out.

Staff deleted the word “major”. Most scientists believe the ozone weekend effect is related to the changes in NO_x relative to weekdays. The real question is how these reductions in NO_x affect the O₃ formation and measurement process. There are almost certainly both positive and negative effects of NO_x reductions on O₃.

Line 24: “Staff is eagerly anticipating the results of modeling applications that are well-designed to test various hypotheses of the cause(s) of the Weekend Effect” seems to imply that models alone will be able to resolve this in the near future. However, the discussion in Chapter 6 discusses the myriad of uncertainties that make this highly unlikely; when one also considers the relative insensitivity of model ozone predictions compared to other species as mentioned earlier, this statement seems out of place. Same comment with respect to the statement at the top of the next page that “Of critical need now is the development of weekend emission inventories... Only then will the weekend modeling results effectively be able to guide the control strategies”. Given the history of emission inventory accuracy and model predictions for O₃, this seems overly optimistic.

Staff clarified the meaning of “well-designed” and modified to not give impression that an accurate WE emissions inventory is all that is needed to begin using models to evaluate the WE effect.

Page C-3: Third line from bottom: “The relative emphasis placed on one precursor or the other is better left to regional planners addressing the specifics of their local situation.” This seems contradict the argument on pages C-34 and C-35 that air pollution control strategies need to be developed on a comprehensive basis.

Staff reviewed and made consistent.

Page C-4: 1st paragraph, line 7: Is the word “thoughts” a typo? Sentence does not make sense.

Staff has fixed.

Page C-5: immediately above table: Finlayson-Pitts, 1993 reference should be Finlayson-Pitts and Pitts. 1993

Staff corrected.

Page C-6, 4a): Mochida (2000) should be Mochida and Finlayson-Pitts (2000) and Saliba (2000) should be Saliba et al. (2000).

Staff corrected.

Again, the data from Stutz et al. in the Phoenix studies will probably shed some light on this issue of carryover in layers aloft.

Staff agrees.

Page C-11: 7a). Again, I think it needs to be emphasized that the ozone isopleths and NO_x quenching are based primarily on **gas phase** chemistry. What we are beginning to learn about heterogeneous chemistry suggests that it may be significant, particularly in the boundary layer where most measurements of criteria air pollutants are made. This is an uncertainty that cannot be ignored or solved by the “next generation of smog chambers” which are often designed to minimize heterogeneous chemistry on walls.

Staff has done.

Page C-13, 11a) last sentence: “Because the NO_x reduction hypothesis ... the NO_x reduction hypothesis will be a leading factor in WD/WE differences”. I am not sure what this means, as it again implies that the other hypotheses are not important when there simply are not the available data to test this properly.

Staff has now separated O₃ quenching from the NO_x reduction hypothesis; this will soften the implication for the NO_x reduction hypothesis.

Page C-24, 20a): Again, even the “state-of-the-art” models do not include the possibility of heterogeneous chemistry that may turn out to be very important.

Staff mentioned.

Page C-26, 24a). I agree with staff response and would also point out the importance of relying on *peer-reviewed literature*.

Staff has done.

Page C-29, 2nd paragraph: It would be appropriate to mention here the formation at night of N₂O₅ from NO₂ and NO₃, and its hydrolysis as a major source of nitric acid.

Staff has done.

5 and 5a): The OH + NO₂ reaction is a major reason for the “NO_x quenching” of ozone, in addition to the NO + O₃ mentioned here.

The commentator implicitly noted the OH + NO₂ reaction – “they [NO emissions] reduce rates of ozone formation by lowering radical concentrations.”

Page C-35, top paragraph: “Historically, in the South Coast Air Basin, the introduction of NO_x control resulted in a slight increase in the relatively low ozone concentrations in the western/coastal region of the basin where anthropogenic emissions were greatest...”. Is this statement really correct? That is, are there data that unequivocally demonstrate this (independent of meteorological effects)? It is not apparent to this reviewer in the data presented in the TSD or SR that this is the case, and I don't recall seeing it discussed elsewhere in these documents.

Staff has dropped statement for lack of documentation at this time.

14a): "The rate of NO_x reductions has always been the same or less than the rate of VOC reductions and staff recommends continued adherence to this approach in light of the viability of potential relevance of the weekend effect to long-term regulatory controls. Staff agrees that local control strategies must be developed that efficiently address the unique characteristics of ozone formation in each area". The meaning of the first sentence is not clear to me and the second seems to contradict the statement on page C-34 and C-35 regarding the need for comprehensive control strategies.

Staff clarified response.

Peer Review of
The Ozone Weekend Effect in California
Draft Staff Report and Technical Support Document

Prepared for
California Air Resources Board

Prepared by
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3 June 2002

Introduction

ARB has prepared reports that review the “weekend effect” in California. The weekend effect is that ozone concentrations are higher on weekends than on weekdays in some locations, despite reductions in precursor emissions on weekends. This effect has been cited in testimony before the Board as a reason to “go slow” on additional NO_x emission controls. The staff report presents 6 explanatory hypotheses for the weekend effect, each of which may contribute to the overall observed effect. Many of the hypotheses are deemed to be “plausible”, but the report indicates there is insufficient information to determine which hypotheses are “correct”.

A peer review of the draft reports is being conducted by researchers at the University of California, at the request of ARB. Although several other scientists are participating in the peer review effort, the comments presented here were developed independently, without consulting with the other reviewers.

Peer Review Comments on Staff Report

I believe that the NO_x reduction hypothesis is the dominant cause of the observed weekend ozone effect, mainly associated with reductions in activity and NO_x emissions from diesel engines. However, the existence of higher weekend ozone levels at some locations does not mean that efforts to control NO_x are or have been counter-productive for ozone everywhere in California. Furthermore, NO_x controls may be necessary to reduce PM_{2.5}, even if this will slow progress in reducing ozone.

In his comments, Dr. Harley identifies the basis for his belief, a basis that is in the process of investigation. Rather than adopt his verdict as a fait accompli, we continue to work through the evidence and its reasonable interpretations.

A1. During the period 1980-2000, the weekend ozone effect has become much more prevalent in California. This extremely important finding about the observed weekend effect is demonstrated clearly in the technical support document, but has been largely ignored in the staff report. This finding should be mentioned prominently in the abstract and executive summary of the staff report, and should be used a **major additional test** to evaluate hypotheses for plausibility in explaining the weekend effect.

The spatial and temporal evolution of the ozone weekend effect will be given more prominence in the final report because it does provide additional insight as to the factors or causes of the weekend effect. Any hypothesis of the weekend effect needs to consider its theoretical consistency with the observed evolutionary temporal and spatial patterns. Information from locations where the weekend effect is small or not observed also can contribute to our understanding of the causative factors. CARB staff has included some analyses of other areas besides the South Coast Air Basin in the report and perhaps more information can be gleaned from them. However, the focus of the efforts was on the SoCAB because ozone concentrations are the highest there, the weekend effect is the strongest there, and the monitoring record is the most comprehensive there.

The spread of the weekend effect to more locations throughout California between 1980 and 2000 is **consistent** with the NO_x reduction hypothesis, because diesel NO_x emissions have increased in both absolute magnitude and relative importance during this period, and diesel engines are known to have large weekday-weekend differences in activity patterns and emissions. The diesel engines (both on-road trucks and off-road sources such as construction equipment) have become an increasingly influential "lever" affecting total NO_x emissions on weekends.

The combination of increasing diesel activity over time and the unique diurnal and weekly patterns of diesel activity is one possible explanation of the increased weekend effect. However, consistency does not prove cause. Another possible explanation is the increased urbanization of many locations where the weekend effect is observed (the weekend effect is only observed in urbanized areas but not necessarily in all urban areas; furthermore, the effect is first observed in the "downtown" or most congested areas). As urban areas (and the associated traffic congestion) have expanded and fresh emissions (particularly from motor vehicles) become more ubiquitous, the effect of ozone quenching by NO has become more ubiquitous spatially and temporally throughout the day. Thus, the ground level monitoring sites throughout the urban areas tend to have ozone concentrations suppressed by the fresh NO emissions throughout the day, including afternoons when ozone concentrations peak.

The NO_x timing hypothesis is **inconsistent** with the observed spread in the weekend effect, because a decreasing fraction over time of the total NO_x emissions (i.e., mainly the LD emissions) gets shifted later in the day on weekends. The diesel NO_x emissions already peak in the middle of the day on weekdays, so they don't shift as much in time on weekends, but rather diesel emissions mainly decrease at all hours on weekends.

The argument above addresses only part of the issue. The NO_x timing hypothesis may not be acceptable as an explanation of the entire ozone weekend effect, but it may still be responsible for a significant part thereof. If so, its contribution may be decreasing over time as Dr. Harley contends. Nevertheless, that contribution may remain important from at least two perspectives. First, Dr. Harley pointed out that the NO_x timing hypothesis should really be "emissions timing." Both VOC and NO_x emissions follow different timing patterns on weekends compared to weekdays. Second, data for mid-day traffic volume in the SoCAB in 2000 is about 20% greater on Saturdays and 2% greater on Sundays compared to mid-week volumes. These differences seem to represent relative increases compared to similar data for 1997 (4% greater on Saturdays and 6% less on Sundays). If Californians are gradually increasing the level of their activity on weekends, the timing discrepancy may be growing (at least with respect to VOC emissions) rather than diminishing.

As Dr. Harley pointed out elsewhere, the NO_x-timing hypothesis should more appropriately be named the "emissions-timing" hypothesis because both ozone precursors are affected by the transition in peak activity from the morning commute to mid-day from weekdays to weekends. As Dr. Harley also points out, the temporal shift is greater for ROG emissions than NO_x emissions because heavy-duty diesel emissions (major NO_x source but minor ROG source) primarily decline from weekdays to weekends rather than shifting later. Thus, the photochemical system during mid-day on weekends would tend to be more sensitive to NO_x emissions than during the normal diurnal transition. The diurnal profile of ozone concentrations (e.g., at Azusa) suggests

that WEs have an extra hour of ozone production during the most effective ozone formation time of the day (plenty of sunshine and emissions).

Given that ozone levels have been declining (presumably not only at the surface but also aloft) between 1980 and 2000 in the SoCAB, the carryover aloft hypothesis is **not consistent** with the spread of the weekend effect to more locations over this time period.

The qualifier, "presumably," is crucial. Ozone aloft may or may not have been reduced as fast as indicated by ozone measurements at the surface. A key factor in the carryover aloft hypothesis is that the ozone-forming system aloft is strikingly different from the measurements available at the surface. Following this path, we believe the spread of the weekend effect to more locations over time is consistent with the carryover aloft hypothesis and with the NO quenching hypothesis, which has been separated out from the NO_x reduction hypothesis since Dr. Harley's review. NO quenching of ozone occurs whenever ozone and fresh NO are present together and is not uniquely a phenomenon associated with the NO_x reduction hypothesis.

The bulk of the ozone molecules formed in the lower troposphere does not occur at the surface but above the surface in a layer of air between 100 and 1000 meters aloft. Data indicate that little NO exists above 100 meters aloft because NO is rapidly converted to NO₂ as it mixes upward. Ozone that forms aloft persists aloft because the quenching by NO there is limited to plumes from aircraft and elevated stacks. Because of the longer residence time of VOC emissions compared to NO_x emissions, ozone formation in this large air mass above the immediate surface layer is likely to be as or more sensitive to NO_x emissions than VOC emissions. Thus, NO_x emission reductions may be needed to accelerate ozone improvements aloft. Furthermore, efforts to reduce the reactivity of VOC emissions have probably pushed their contributions to ozone formation further downwind (horizontally or vertically) or later in time and perhaps increasing relative carryover to the following day.

The NO quenching hypothesis may be a key factor in the spatial growth of the weekend effect. In the South Coast and the S.F. Bay Area, population growth and VMT have grown greatly over the last two decades. This growth has been especially noteworthy inland because the coastal regions were developed earlier. As commercial growth has pushed further east, surface NO emissions in the inland regions have increased. These NO emissions should destroy more ozone near the surface on weekdays than they do on weekends. The pattern of increasing numbers of sites exhibiting the weekend effect has steadily incorporated sites further and further inland in high growth areas.

To summarize, although the amount of precursors being carried over is likely declining (countered by lower VOC reactivity) and O₃ concentrations aloft are probably declining too, the expanding, ubiquitous nature of NO emissions at the surface (smaller total amount but spreading over larger area) causes the O₃ quenching effect to become relatively more abundant, destroying a larger fraction of the ozone that forms before it can reach the surface, especially on weekdays. Together, carryover and urbanization cause more sites in downwind regions to display the weekend effect.

A2. Hypothesis #2 (NO_x-timing) is inappropriately named and described. It would be better to call this an "Emissions timing" hypothesis. It seems unlikely though that shifting VOC emissions later in the day would increase ozone. The timing of CO and VOC emissions (almost all from light-duty vehicles) is more affected on weekends than the timing of NO_x. This is because heavy-duty diesels are an important and growing source of NO_x emissions, with a different diurnal pattern of activity and emissions from LD vehicles. Dreher and Harley (*J. A&WMA*, vol. 48, pp. 352-358, 1998) and ARB staff (p. 5.1-5 of TSD) agree that diesel truck activity on weekdays has a broad mid-day peak in activity. Therefore a large portion of NO_x emissions already occur in the middle of the day on weekdays. The synopsis on p. 2-5 of the NO_x timing hypothesis asserts that NO_x emissions occur on weekends into a more "mature photochemical system". This is not true if VOC emissions are also shifted later in the day on weekends. The main NO_x emissions that are shifted in time on weekends (from LD vehicles) are co-emitted with VOC that also gets shifted.

Professor Harley is correct in noting that VOC, NO_x, and CO emissions associated with motor vehicles shift from the weekdays to the weekend. As he intimates, the shift in VOC emissions would have a smaller effect on peak O₃. It is likely that the timing shift would be more influential for NO_x impacts because of quenching and greater sensitivity to NO_x at midday. Thus, we refer to the hypothesis as "NO_x timing". Professor Harley points out that the NO_x timing effect is counteracted by the large decline in heavy-duty diesel truck activity on weekends (normal weekday peak is around midday). NO_x emissions from diesels have continued to make up an increasing portion of the on-road NO_x emissions (> 1/3 in 2000). It is because the diesel emissions make up an increasing portion of the NO_x emissions that the shift to midday in gasoline emissions makes that atmosphere even more sensitive to NO_x (similar biogenic VOC and light duty vehicle emissions but less diesel NO_x than on weekdays). The timing difference may not account for the entirety of the weekend effect, but it may still contribute significantly.

The "more mature photochemical system" to which we refer is the full photochemical system up to about 1000 meters. At mid-day on a weekend, this system differs markedly from the mid-day system on weekdays. The limited emissions from the morning hours on a Saturday or Sunday have already "cooked" for several hours and have a relatively higher NO₂: NO ratio. Materials that carried over aloft are already "aged" and form a larger fraction of the photochemical soup on weekends than on weekdays because fresh emissions on weekends are much reduced. In addition, the NO_x reduction hypothesis asserts that the early morning NO_x emissions serve to depress photochemistry by reacting with hydroxyl radicals, and presumably, this phenomenon is less prevalent on weekends.

The DRI evidence (Fujita et al., 2002) seems clear that mid-day fresh emissions on weekends enter a system that tends to be "hotter" compared to the system that prevails at mid-day on weekdays.

A3. The soot and sunlight hypothesis is inappropriately named. A better name would be "aerosols and UV radiation". The text on p. 2-13 incorrectly implies that soot particles only absorb sunlight, whereas in fact these particles both scatter and absorb light. Furthermore, soot may not be the only UV-absorbing component of aerosols. Organic carbon species can absorb in the UV (e.g., aromatic rings). In addition, fine particles including secondary nitrates and sulfates may serve as condensation nuclei for fog and

cloud droplets, which in turn can reflect sunlight back to space. Therefore there may be both direct and indirect effects of aerosols on UV radiation and photochemical reactions.

Though "soot and sunlight" has poetic appeal, Dr. Harley makes a convincing case for renaming this hypothesis "aerosols and UV-radiation".

A4. The inference that ARB's strategy of controlling both VOC and NO_x has been more effective in reducing ozone than a strategy of controlling VOC emissions alone is not supported adequately in the report. The success of ozone control efforts in the South Coast Air Basin does not by itself prove that the strategy of controlling both VOC and NO_x has been optimal. Even if control of both pollutants is warranted, it is not clear that the relative emphasis on VOC vs. NO_x control has been optimized.

For the purpose of devising emission reduction strategies, we often rely on air quality models, which integrate the "science" and offer great flexibility. However, staff notes multiple reasons in this report why today's state-of-the-art models are likely to overlook ozone-reducing benefits of NO_x reductions. Since staff does not believe models are completely trustworthy for determining optimality, it is valid to examine the success of the combined VOC and NO_x reduction strategy at various places in California.

The dramatic success achieved in the South Coast coincides with the greatest relative NO_x reductions. The S.F. Bay Area had somewhat lower relative NO_x reductions and achieved somewhat less progress. The Sacramento Metropolitan Area and the San Joaquin Valley had later and lesser NO_x reductions and have achieved very little progress. Of course, these areas differ from one another in many other respects, including prevalence and distribution of various emission sources along with major differences in meteorological conditions. Nevertheless, the real world data can be assembled scientifically and rationally to form a picture that indicates that more, not less, NO_x controls are needed to further reduce ambient ozone concentrations.

Results of simulation models are not credible enough to vacate staff's view of the empirical evidence based on regional trends and WD/WE differences.

B1. Figure 2-4 (on p. 2-18) reflects diurnal patterns for LD traffic only. HD traffic follows a different pattern on weekdays (see Dreher and Harley, 1998; also see for example Figure 5.1-27 in Chapter 5 of the TSD).

The figure actually represents all freeway traffic together, light-duty and heavy-duty. Dr. Harley makes a very good point, however, that the day-of-week patterns for heavy-duty vehicles do not look like the figure; the volumes of light-duty vehicles overwhelm them. Staff has inserted a reference to TSD Chapter 5.1 for separate figures representing light-duty and heavy-duty traffic.

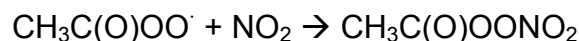
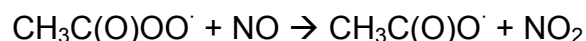
B2. On p. 2-4, I believe the stated diesel contribution to total on-road vehicle NO_x emissions is too low (the text claims only 30% of the total was diesel as of 1997).

Staff has double checked the emission numbers with the latest estimates and updated the text to reflect the greater diesel contribution to total NO_x emissions (35%).

B3. On p. 1-5, the assumption that meteorology is unaffected by day of week is contradicted on p 1-7 where a "small day-of-week influence was noted for aerosol concentrations *and ambient temperature*".

Staff rephrased the material slightly. The general, and commonly accepted, assumption is that, on average, the meteorology on weekends will be the same as on weekdays. The UCLA analysis did note a small temperature effect, which may or may not be real (i.e., statistically significant). This observation may relate back to the diurnal variations in aerosols and additional work is needed to verify and quantify the range of aerosol impacts.

B4. Peroxyacetyl nitrate (PAN) should be dropped from the list of pollutants for which NO_x emission controls are automatically assumed to be beneficial. In Figure B.10 of Harley (1996), a 50% reduction in NO_x emissions in the SoCAB is shown to cause large increases in levels of PAN. The staff report asserts that NO_x controls will have benefits for PAN, without providing any supporting evidence. The relevant chemistry includes a key pair of competing reactions:



The first reaction competes with PAN formation; if peroxyacetyl radicals follow the first pathway, they are permanently removed and no PAN is formed. The relative amounts of NO and NO₂ present (in addition to the absolute concentration of NO₂) affect changes in PAN as NO_x emissions decrease or increase. This issue arises in the abstract (page vii), executive summary (page x), and page 4-2 in conclusion #3.

Reference: Harley, R.A. (1996). Impact of Improved Emissions Characterization for Nitrogen-Containing Air Pollutants for the South Coast Air Basin. Report to ARB, contract 93-310.

PAN is a NO_x product but, as Dr. Harley points out, its formation and removal are complicated non-linear processes. Staff rewrote the material to avoid the impression that NO_x emission reductions automatically reduce PAN concentrations. The reference to PAN in most of these sections however is to its health concerns rather than its formation processes.

On the same pages of the staff report cited above, it should be noted that in most of the state, PM nitrate concentrations are highest in winter months, whereas ozone is high during the summer. This may present opportunities for seasonal control of some stationary source NO_x emissions. The importance of carbon particles as a contributor to PM_{2.5} mass also should be acknowledged.

Although the cooler, moister conditions during winter promote more PM-nitrate, PM-nitrate is also significant during the summer in the SoCAB. From a mobile source control perspective, seasonal control is not a viable option. However, staff has noted the potential, though small, of

seasonal controls on some stationary sources. Staff has also noted the contribution of carbon particles.

B5. In the last paragraph of p. 1-4, it is stated that VOC-only control plans are in place in air basins other than South Coast. This is not correct. The Bay Area implemented a major program of retrofit controls and new source rules on stationary sources of NO_x through the 1990s. Though the staff report indicates there is an overall decrease in Bay Area ozone over a 10-year period, most of the decrease occurred in the late 1980s before the NO_x control program began. Since then there has been no significant downward trend in ozone levels in the Bay Area.

NO_x reductions have occurred in all areas of the State due to the motor vehicle program and the local air pollution control districts have emphasized NO_x reductions to varying degrees. Staff has better documented the basis for the statement in its redraft of the report.

B6. The issue of uncertainties in chemical mechanisms under low-NO_x conditions is mentioned in the executive summary on page xxi. I understand this concern to relate to rural conditions with extremely low NO_x levels, where radical-radical recombination reactions to form peroxides are favored over NO → NO₂ conversions. I don't think this concern applies in the context of weekend decreases in NO_x emissions within urban areas where NO_x levels remain high on all 7 days of the week.

Staff may have used the "low-NO_x" term liberally in this instance. What staff is concerned about here is the ability of photochemical models to accurately simulate real world conditions when NO_x concentrations are less than about 5 ppb. This concern arises out of the routine, non-specific measurements of NO₂ and other higher oxides of nitrogen – the imprecision of ambient measurements and the uncertain impacts that the relative mix of these compounds and heterogeneous chemistry have on ozone concentrations is not well known. As the emissions in an air mass age and the air mass is separated from sources of fresh emissions, what are the effective VOC/NO_x ratios and what are the effects on ambient ozone concentrations? Also, at low VOC concentrations and low VOC/NO_x ratios, is the shape of the constant ozone lines in "EKMA-type" diagrams vertical (i.e., no NO_x inhibition/disbenefit effect) or do they bend back (i.e., zone of disbenefit)? Until more laboratory and field experiments, and modeling simulations are performed to understand the chemistry in these relatively clean conditions that characterize the large air mass from a few tens of meters to several hundred meters above the ground, we cannot fully appreciate the impact of this potentially large reservoir of air and ozone. Limited measurements of NO_x in this regime indicate that mixing ratios are low and very little is in the form of nitric oxide.

B7. Much is made in the staff report and TSD about the difference between periodic (i.e., weekend) versus steady or "strategic" reductions in emissions on all days. I believe the distinction is of little relevance for the urban scale where the residence time of air is short. Urban-scale air quality modeling (and even regional-scale modeling for central California) shows little sensitivity to initial conditions after a 1-day spin-up period. The staff report overplays this issue on p. xv of the executive summary.

Professor Harley's comment here relates to the root assumption by many that the transition from a weekday pattern of emissions to a weekend pattern is a natural experiment of the impact of NO_x controls. Modeling runs usually have a 1-2 day spin-up period to minimize sensitivity to assumptions about initial conditions and to have the results based upon the recent pollutant emissions. However, that does not necessarily mean the model is only sensitive to emissions during the last day nor that the model faithfully simulates the real world conditions, particularly in the air above the ground level measurements biased by fresh emissions. This comment presumes that ozone precursor emissions (especially NO_x) react out of the photochemical system rapidly. Although some scientists believe that a day's ozone peak is primarily related to the emissions during that morning, more profess that the highest ozone concentrations occur after multiple days of build-up. The fact that global and regional ozone concentrations appear to be increasing is counter to the premise that previous conditions do not matter much. New implications of heterogeneous reactions also need to be fully evaluated. Staff still believes that a given concentration has a context (history).

C1. In Table 1-9, the change in other (Light-duty?) vehicle NO_x emissions between 1995 and 2000 looks too large compared to corresponding changes in CO and VOC shown in the table. Field measurements at the Caldecott tunnel indicate that NO_x is not decreasing as rapidly as VOC and CO from LD vehicles. Diesel NO_x is likely to be increasing over this period. The table also uses confusing terminology. On-road and off-road mobile sources are not clearly identified or separately.

Professor Harley's concerns appear valid and staff verified and clarified the information presented in the table.

C2. On page 2-4, expectations of ozone sensitivity for VOC/NO_x less than 8 are mentioned. Earlier in the text on p. 2-2, more caution is used in extrapolating from results of smog chamber studies to the ambient atmosphere (a range of 8-10 was cited).

Staff made the statements consistent.

C3. On page 1-2, the global background ozone level in the troposphere, in the absence of human activities worldwide, would be expected to be lower than 40 ppb. A range of 20-40 ppb is cited, and the whole range seems too high absent the human-induced changes in background tropospheric chemistry.

Staff has modified the discussion to clarify differences between pristine global background ozone concentrations and anthropogenically impacted regional background concentrations.

C4. Also on page 1-2, oxygen (O₂) accounts for ~21% of air molecules (dry basis), whereas the text incorrectly claims 18%. On a mass basis, the oxygen fraction is higher than 21%. If you want to include water vapor which is variable, the oxygen percentage might drop as low as ~20% under very humid summer conditions.

Staff corrected this error.

Peer Review Comments on Technical Support Document

Chapter 1: Characterization of Ozone Weekend Effect

By examining the 2nd through 11th highest ozone days in the SoCAB for the period 1980-1998, it is found that the weekend effect is becoming more widespread over time.

Weekday-weekend differences are found to be larger on “moderate” days, with a smaller effect noted on the days that are most conducive to high ozone levels.

The effect is characterized as “relatively small” (<10% on p 1.2-5) on the highest-ozone days. Note that this may be too optimistic when 8-h average ozone concentrations are considered. Marr and Harley found the weekend effect was more pronounced when 8-h avg ozone concentrations were examined.

Staff's analysis of the magnitude of the weekend effect on 8-hour ozone concentrations indicated that it is comparable, though slightly higher, to the weekend effect observed with 1-hour concentrations. Because the long-term trends for the 1-hour and 8-hour concentrations have been similar and because the daily 1-hour peak typically occurs within the 8-hour peak, staff limited the presentation to 1-hour concentrations. Dr. Harley's point is well-taken and a synopsis of the weekend effect with respect to 8-hour ozone concentrations is presented in the following table. As can be seen, the ozone weekend effect is comparable (slightly higher) for 8-hour concentrations than 1-hour concentrations. As with the 1-hour concentrations, the weekend effect is smaller in the downwind areas with higher O₃ concentrations.

Analysis of Daily Max 8-Hour Ozone			
<u>District</u>	<u>Years</u>	<u>% Change Sun./Fri.</u>	
		<u>All Sites</u>	<u>Downwind</u>
Bay Area AQMD	1992 - 1994	16.4%	11.8%
	1996 - 1998	19.9%	16.2%
	1998 - 2000	29.2%	27.5%
South Coast AQMD	1992 - 1994	14.6%	5.2%
	1996 - 1998	23.0%	15.1%
	1998 - 2000	27.6%	26.9%
San Joaquin Valley Unified APCD	1992 - 1994	4.2%	1.8%
	1996 - 1998	7.3%	4.4%
	1998 - 2000	8.3%	4.4%

For the SJV (section 1.3), it would be helpful to include a map showing site locations. I prefer the organization of sites by sub-region to the alphabetical listing. Marr and Harley report the weekend effect becoming significant in the northern SJV in the 1990s.

The suggested modifications would help the reader and have been incorporated into the final report.

In section 1.4 (specifically 1.4.4.1), further results are presented indicating that the weekend effect is spreading in the SoCAB to sites farther downwind over time.

Staff specifically noted the expanding nature of the ozone weekend effect in the Introduction to the Staff Report.

Chapter 2: Analysis of Variations in Ozone and Precursors

In section 2.1, I prefer that the ratio be calculated and referred to as NO_y/NO . This has the advantage that instrumental loss of precision in subtractions to give “ NO_2 ” by difference between NO_x and NO are eliminated. Furthermore, the NO_2 measurement is not truly NO_2 because other species such as PAN are included in the measurement. The NO_2/NO ratio figures in the photostationary state relationship for ozone, although other factors such as solar actinic flux and temperature would need to be included for a complete analysis.

Professor Harley's points are valid but are not addressable because the NO_y monitoring network is very limited and the monitors are difficult to operate. Furthermore, the NO_y measurement would also include additional species. Although erratic and uncertain at low concentrations, the NO_2/NO ratio provides a crude estimate of whether fresh emissions (ozone quenching) or photochemistry is predominating in the atmosphere where the measurements are being made.

On p. 2.2-8 I note again that the TSD indicates the weekend effect is growing stronger and more widespread over time.

In section 2.3, why was the analysis limited to the SoCAB only? I believe PAMS or other similar data are available in some other parts of California. On p. 2.3-1 there is an inconsistency in the abstract: 3-hour can samples are mentioned, and then a 4-hour averaging period from 8:00 to 12:00 is described.

Staff limited the analysis to the SoCAB. Although PAMS data are available in other areas, the data are not as extensive. Staff corrected the averaging period (i.e., 8:00-11:00).

In section 2.4, finding #2 on p 2.4-2 concerning small decreases in HC reactivity applies consistently to all 3 sites for 1995 data, but is not consistent with all of the results for 1996 (two AM sites and one PM site show HC reactivity either increases or stays about the same from weekdays to weekends).

Staff believes “appears to be slightly lower” is a succinct and accurate summarization of the data shown but has added the word “generally”.

It should also be noted that in the SoCAB the phase-in of Federal RFG had already taken place in summer 1995, so that some of the changes in HC speciation such as the widespread introduction of MTBE had already taken place. A comparison between 1994 and 1996 might reveal larger changes in HC composition and reactivity, though appropriate data are probably not available from 1994.

Professor Harley makes a valid point and is correct in noting that no special measurements were made in 1994 to assist the evaluation.

In section 2.5, it would be appropriate to mention that the KI sampler used in the ozonesondes responds to oxidants other than ozone. On p. 2.5-5, I agree that air flow is complex along the coast of the southern California, especially in the boundary layer. However, at higher elevations (specifically, above the planetary boundary layer) the flow becomes more organized and is driven by synoptic-scale pressure gradients.

Staff articulated that ozonesondes respond to multiple oxidants not just ozone; however, ozone is the dominant pollutant measured. Synoptic-scale pressure gradients will tend to drive the air flows aloft but when the pressure gradients are weak, the complex effects of meso-scale processes become more evident.

A general comment on this section is that the long-term drop in ozone levels between 1980 and 2000 should lead to diminished potential for carryover aloft. In contrast, the weekend effect has spread during this period.

This is a critical point in the evaluation of factors/causes contributing to the increasing spatial coverage of the ozone weekend effect. If ozone aloft is simply due to the advection or transport of surface ozone concentrations as the air moves and/or is mixed, then the decreasing ozone concentrations at the surface over time should also have resulted in decreasing ozone concentrations aloft. However, if ozone is being formed aloft, then the concentrations aloft are not necessarily a direct, linear function of the ozone concentrations at ground level. Because ozone concentrations aloft are not routinely monitored (only during special field studies with an emphasis on episodes resulting in peak ozone concentrations at the surface), relatively little is known about the atmospheric processes in the large volume of air between about 100 meters and 1000 meters that frequently (almost every day in locations inland from the coast) mixes and interacts with the ozone and emissions observed in the lowest 10 meters of the atmosphere. The chemistry in the air aloft is likely to be very different from the chemistry in the lowest layer where fresh ozone precursors are continuously being emitted (and NO in particular as it temporarily suppresses ozone concentrations). In the measurements that have been made aloft, ozone concentrations in the SoCAB are seldom less than 50 ppb and almost always greater than the surface ozone concentrations. This is a huge reservoir of ozone and ozone precursors that can influence the mid-day surface ozone concentrations and the photochemistry when the increasing atmospheric mixing taps into the air mass aloft.

Chapter 3: Variations in Particulate Matter

Day-of-week differences in particulate matter have two important links to the present weekend effect report: (1) reductions in PM nitrate are cited as a major rationale for NO_x controls, even if such controls might slow progress in reducing ozone levels in some locations; (2) a “sunlight and soot” hypothesis has been suggested as a possible contributing factor to the overall weekend effect.

The assessment of day-of-week differences in particulate matter concentrations is challenging for several reasons. First, much of the historical PM data consists of 24-hour air samples collected on filters once every 6th day, with PM₁₀ mass determinations only. Second, variations of PM-generating processes (e.g., wood-burning in fireplaces, forest fires) on longer time scales may introduce seasonal variability that greatly exceeds day-of-week variations. Finally, the PM constituents of most interest here are PM_{2.5} nitrate, and all particles in the 0.1-1 μm size range, whereas most of the PM measurements do not provide the appropriate size or chemical resolution.

I recommend further research on these questions should give special attention to measurement methods that provide high-time resolution data on PM nitrate, carbon particles, and light scattering and absorption by aerosols. Measurements of aerosol effects in the UV are essential if the “sunlight and soot” hypothesis is to be tested in a meaningful way.

On p. 3.1-6, there is a statement that “[current instruments] do not permit analysis for ionic and elemental constituents”. I disagree for nitrate – see the paper by Stolzenburg and Hering (*Environ. Sci. Technol.*, vol. 34, pp. 907-914, 2000), and more than a year of semi-continuous PM nitrate data now available at Fresno.

Staff concurs that instrumentation has been developed in recent years and that data collected since the first draft of this report (e.g., California Regional Particulate Air Quality Study, PM Super Sites) will enable improved day-of-week analysis for nitrates. Staff is publishing some results in the July 2003 issue of the Journal of the Air & Waste Management Association. The results presented there indicate that nitrate concentrations on Saturday are among the highest of the week while concentrations on Sunday are among the lowest of the week. Day-of-week continuous PM_{2.5} mass generally follows the same temporal pattern as CO and NO_x, with Sunday having the lowest concentration.

I believe useful additional evaluation could be performed on the “sunlight and soot” hypothesis by examining aerosol UV optical depth data by day of week measured at Riverside and Mt. Wilson during SCOS97, and similar continuous data available for ~5 years at Davis.

Although information can be gleaned from short-term special studies such as SCOS97, staff believes that longer records such as from Davis will be more definitive.

Chapter 4: Toxic Contaminants

I did not review this chapter of the TSD.

Chapter 5: Vehicle Activity Patterns

The meaning of “circumstantially consistent” at the bottom of p. 5.1-1 is unclear.

Staff has edited the sentence to be clearer (e.g., “Overall, the general patterns in the WIM data are consistent with Hypothesis #1, Hypothesis #2, Hypothesis #3, and Hypothesis #4”).

The value of counting surface street traffic seems questionable to me, given that long-haul diesel truck traffic occurs mostly on the state highway system, and that a fraction of surface street LD vehicle traffic would be expected to correlate with freeway traffic since these vehicles must use surface streets at some point to access the freeways.

Staff believes that acquiring representative counts of surface street traffic is a critical component of definitively addressing the ozone weekend effect. Obviously, the long haul diesel traffic primarily occurs on the freeways. However, many goods and products are then shipped from distribution centers to retail points of sale via HD diesel trucks (e.g., grocery stores, restaurants, fueling stations, shopping malls). Many of these will go from one delivery point to another via surface streets. In addition, construction vehicles (e.g., gravel & dirt trucks, cement trucks, materials delivery trucks) operate an appreciable amount of miles on arterial roads. Regarding LD vehicle activity, traffic on arterial roads near freeway access points probably is highly correlated with freeway activity. On the other hand, activity on portions of arterial roads not adjacent to a freeway may not be highly correlated. Based on personal experiences, staff suspects that many local trips (e.g., school, park, grocery store, department store, restaurant, worship centers) never access the highway, especially on weekends. Additional analysis and data collection are needed to quantify surface street activity, especially around mid-day, and to compare with freeway activity. CARB currently has two activity contracts (e.g., traffic counts around a few monitoring stations, WIM data, and tens of residential vehicles with GPS units) that will help address the suitability of WIM data from freeways for characterizing the vehicular activity on surface streets.

Chapter 6: Modeling Issues

I was surprised and disappointed to find that no air quality modeling **results** were presented in Chapter 6 of the TSD. Such results might have helped to inform the analysis of the weekend effect and its causes. While I agree there are many challenges to overcome when applying air quality models to study the weekend effect, many of these challenges also arise in other applications where air quality models are used. A modeling study such as the one envisioned in Chapter 6 has been described by Linsey Marr in her Ph.D. dissertation at UC Berkeley. Linsey developed separate weekday and weekend gridded estimates of vehicle emissions using weigh-in-motion traffic counts and other data, and conducted an air quality model performance evaluation for 3-6 August 1990 (Friday through Monday) in Central California. Various hypotheses that might contribute to the weekend effect were investigated, with the

finding that the changes in NO_x mass emissions on weekends were more important than changes in emissions timing in explaining weekday-weekend differences in ozone concentrations.

Although models are useful tools for assessing potential effects and attempting to quantify the impacts of changes, they are not inherently research tools because they cannot incorporate all the chemical and physical processes that occur in the real world environment. They are simplified approximations of what scientists believe are the dominant factors influencing what we observe. While helpful approximations, models have some serious limitations and potential biases for addressing the weekend effect. Among these limitations are 1) accurate, gridded, day-of-week diurnal profiles for emissions, 2) realistic mixing algorithms for the movement of pollutants between layers in the model, 3) accurate low NO_x chemical reactions in the proportionately large air mass from a few tens to several hundreds of meters above the earth's surface, 4) lack of potential renoxification mechanisms, and 5) in coastal areas, the lack of halogen chemistry.

On page 6.1-8, see previous comment B6 on the meaning of low-NO_x conditions.

See also response to comment B6.

Chapter 7: Recommendations

I disagree with the recommendation that another major field study in the SoCAB is needed as a top priority (p. 7.1-1). Any short-duration field study is likely to be confounded by meteorological variability that can lead to changes in ozone levels much larger than changes associated with the weekend effect. There is also much that can still be learned (at significantly lower cost) by further analysis of SCOS97 and other existing data.

To address all unknown or poorly characterized features of the weekend effect at the same time would require a major field study. However, some features could be targeted independently in smaller, focused studies. Undoubtedly, short-term studies are subject to the vagaries of meteorology that could obscure or even contradict the actual air quality effects. Staff also concurs that the existing data could be analyzed further to provide additional insights into the weekend effect. Given other commitments and the current budget crisis, CARB staff is beginning to plan for some focused studies in the 2005-2007 time frame.

The recent experience with major field studies (both SCOS97 and CCOS) has highlighted difficulties that arise when targeting high-ozone days using the "intensive operating period" model. Both of these multi-million dollar efforts encountered unusually low ambient ozone concentrations throughout the periods of study. For the future, I recommend permanently augmenting routine monitoring sites with additional, reliable instruments running all the time that provide a long data record and cover additional pollutants continuously such as total NMOC, VOC speciation, PM_{2.5} mass, and major chemical constituents of PM_{2.5} (e.g., nitrate, sulfate, carbon).

Professor Harley correctly notes the strong influence of meteorology and the limited success in capturing air quality episodes with high concentrations. The long range planning for a field study and the interannual variations in conditions associated with variable effects associated

with general patterns (e.g., El Niño), make capturing peak episodes difficult – a problem that will only become greater with improving air quality and with the variability associated with global climate change. The “intensive operating period” model is not inherently flawed as it does tend to capture the episodes with the highest concentrations observed during that particular year. In the case of investigating the weekend effect, we are not as interested in capturing peak ambient concentrations for the year as we are in looking at relative differences in composition of the air between different levels (i.e., at the surface where our routine air sampling occurs and in the thick layer of air between tens and hundreds of meters above the ground which routinely mixes and interacts with the distinctively different surface layer of air. Undoubtedly, the routine measurements in the surface layer of air would need to be enhanced but the main focus needs to be on acquiring “routine” measurements of air quality above the surface layer of air to identify the relative differences with the surface air and the atmospheric processes at work. Focused studies to address issues pertinent to evaluating the various hypotheses of the weekend effect do not need to capture the extreme conditions. A summertime study focusing on the Friday through Monday transition would capture a suite of real-world conditions and enable an assessment of the weekend effect under a variety of conditions contributing to the mean effect.

There is a general recommendation about the need to improve emission inventories, especially for weekend conditions. The recommendation should be explicit about the need to focus on improving characterization of heavy-duty diesel engine activity and emissions. Diesels are a major and rapidly-growing source of NO_x, they exhibit large weekday/weekend differences (as discussed in Chapter 5 of the TSD), and they are poorly represented in current travel demand models and gridded inventories used in photochemical modeling studies.

As the planning evolves, more detailed and focused efforts will be given to HD diesels because of their increasing contribution to the NO_x inventory and their distinctly different diurnal and day-of-week activity patterns.

On p. 7.1-3, I disagree with the recommendation to limit studies of the weekend effect to the SoCAB only. Though ozone control strategies appear to be working in the SoCAB, other parts of the state (especially the San Joaquin Valley) are not making good progress, and we urgently need to understand why. In comments relating to Chapter 6, I summarized the topics addressed in Linsey Marr's doctoral dissertation: statewide spectral analysis of ozone and precursor concentrations, and air quality modeling in Central California. I believe useful conclusions were reached in that research, counter to the claim on p. 7.1-11 that studies of the weekend effect outside the SoCAB are sure to be inconclusive and a waste of scarce resources.

With regard to studying the weekend effect, the SoCAB provides the most comprehensive, routinely collected data upon which to build additional measurements. Furthermore, the weekend effect has grown and is most definitive in the SoCAB. However, Professor Harley is correct in noting that additional study of areas where the weekend effect is weak or missing and air quality trends are different will provide useful information and insights into the likely causes of the weekend effect.

Weekend Effects Peer Review

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Summary

The so-called weekend effect has become an important regulatory issue, especially as it pertains to the control of NO_x emissions. The Staff Report (SR) and Technical Support Document (TSD) reviewed here are high quality documents that succinctly lay out possible causes of the weekend effect, together with an extensive discussion of relevant data and a proposed research plan. The comments provided in this review of the SR and TSD have several major foci:

- What is the relationship between the substantial drop in O₃ in the South Coast Air Basin (SoCAB) and predictions of O₃ levels resulting from the emissions reductions that were implemented? An answer for this question may be imprecise due to data limitations, however, some attempt should be made to reconcile the apparent contradiction between VOC-limited O₃ formation implied by the weekend effect and the fact that the largest drops in O₃ exceedences have coincided with periods of greatest NO_x reductions. Before the current regulatory policy of reducing NO_x and VOCs in approximately equal amounts can be changed, the notion that less NO_x controls would have delivered even cleaner air needs to be firmly established. (Sect. 2.1)

Staff concurs. Professor Paulson has succinctly identified the crux of the weekend effect debate. One potential, and even likely, factor contributing to the ozone weekend effect is the greater reduction in NO_x emissions than VOC emissions on weekends. If this hypothesis is correct and NO_x reduction is the primary causative factor in the ozone weekend effect, and if the ozone weekend effect is representative of the long term effect of NO_x controls on ozone air quality, then the implications are that NO_x controls have been detrimental to the expeditious attainment of the ambient air quality standards. However, long term trends of O₃ air quality and NO_x emissions and air quality suggest that most of the O₃ improvement occurred during the period of greatest NO_x reductions. Staff embarked on the investigation summarized in this report to better understand the O₃ weekend effect, its contributing factors, and the implications for the need of future NO_x controls.

- An alternative mechanism for the influence of carryover aloft in steady vs. periodic NO_x controls is proposed. Carryover aloft likely contributes 20-35% of surface level ozone, and much of this O₃ may be generated under NO_x limited conditions aloft. NO_x controls are particularly effective in reducing this source of O₃, and may be responsible for some of the dramatic improvements over recent years in weekend (and weekday) O₃, in the face of a surface-level NO_x disbenefit. (Sect. 2.2).

Staff concurs. Once again Professor Paulson's perspective is very similar to staff's perspective.

- The VOC/NO_x ratio is an imperfect indicator of VOC or NO_x limitation of O₃ formation, and different indicators may provide better insight to VOC or NO_x limitation of O₃ formation (Sect. 2.3.3). VOC/NO_x ratios of 4-9 in SoCAB are reported in the SR and TSD; the low end of this range is assumed to indicate strong VOC limitation and the high end combined NO_x and VOC limitation. Section 2.3 discusses available measurements of total VOC levels, which show that VOC levels derived from the sum of individual peaks in PAMS type data underestimate substantially total VOC concentrations by 20 to 70%. As indicated in the SR, NO_x is likely overestimated due to the problem with NO_z (= NO_y – NO_x) species being partially detected as NO_x. These results suggest that VOC/NO_x ratios are substantially higher than 4-9.

Staff concurs with Professor Paulson's points.

- There has been heavy emphasis on the analysis of average conditions in the SR and TSD and in much of the ongoing weekend effects research. More emphasis on high ozone days is suggested.

Staff included some analyses looking at the magnitude of the weekend effect on days with different potential for high O₃ concentrations and found that the weekend effect was smaller at higher concentrations where greater health effects occur and the design basis for future controls to attain ambient air quality standards. The difficulty with analysis of the high O₃ days is that the statistics become weaker due to the smaller number of observations and questions of the representativeness for other types of conditions arise.

- The shift in the spatial distribution of emissions between weekends and weekdays can likely explain some of the weekend effect and should be added as one of the hypotheses.

Professor Paulson makes a reasonable suggestion for a spatial distribution hypothesis. Staff has somewhat lumped this day-of-week variation with the NO_x timing hypothesis but it is a separate factor. The difficulty is that staff has little information to go by to characterize the spatial shift in activity. CARB has a contract to collect some vehicles instrumented with Global Satellite Positioning systems to address the shift in residential driving activity patterns but it will be limited in scope. Eventually, when better characterization of the variations in spatial activity is available and the performance of a photochemical model has been thoroughly validated, the spatial hypothesis will be properly tested and evaluated.

1. Introduction and Overview

The Staff Report (SR) and companion Technical Support Document (TSD) cogently lay out several hypotheses for the causes of the so-called weekend effect. The SR is an accurate summary of more extensive the technical support document (TSD). The SR and TSD present available relevant data that is either supportive or inconsistent with each hypothesis, together with corresponding levels of certainty. The SR also addresses to an appropriate degree the major related health issues that are heavily impacted by decisions regarding control of O₃: levels of hazardous air pollutants (HAP's) and particulate nitrate. The reports also propose an 18 month-long field program and a targeted series of modeling and laboratory studies aimed at elucidating the causes of the weekend effect. The plan is an excellent starting point for a program that is likely to generate the information necessary to make accurate predictions of future regulation scenarios.

The ARB's openness in the review process and its tireless pursuit of the best policy based on solid science is to be admired. Further, the authors of the SR and TSD should be congratulated for their success in developing a coherent, high quality document detailing this very complex phenomenon.

This review is organized as follows. Section 2 addresses general topics that appeared as themes in the SR and TSD (and appendices), or on-going weekend effects research. This section contains most of the substantive comments. Specific comments on individual sections of the weekend effects report are provided in Sections 3 and 4. References are provided in Section 5. Minor editorial suggestions have been provided to ARB staff separately.

General Comments

General comments are divided into seven sections: 1) The predictability of the O₃ trend over the past two decades; 2) The potential role of carryover aloft in the observed decreases in O₃ over the past two decades; 3) The HC/NO_x and evidence for VOC vs. NO_x limitation of O₃ formation; 4) the emphasis in the report and in the on-going research on averages; 5) Isopleth diagrams; 6) The NO_x disbenefit; and 7) The spatial shift in emissions between weekdays and weekends.

2.1. The Historical Drop in Ozone Exceedences: Were They Expected?

The complexity of the weekend effect is clear from its many apparent contradictions. Surface level O₃ production appears to be somewhat VOC limited much of the time. Despite a predicted NO_x disbenefit under VOC controlled O₃ formation, substantial O₃ decreases on both weekends and weekdays have been greatest when NO_x controls have been most stringent. According to data presented in Appendix C, the 5-year drops in ROG emissions have been fairly constant since about 1985, at about 23%. During this period, NO_x emissions have been dropping at an increasing rate, from 7% between 1985 and 1990, to 17% between 1990 and 1995 and 18% between 1995 and 2000. The number of days exceeding the O₃ standard has dropped more when NO_x controls have been more stringent; from 25 days between 1985 and 1990 to 39 days between 1990 and 1995 and 61 days between 1995 and 2000. Further, considering individual sites, *Blier and Winer* [1996] found that the largest decreases in early morning

NO_x were associated with the largest decreases in maximum O₃ recorded on the 10 highest days in the 1991-1993 period compared to the 1986-1989 period.

The core question motivating the weekend effect studies is the relative efficacy of hydrocarbon and NO_x regulatory controls. There is little doubt that lower NO_x emissions on weekends results in higher O₃ on weekends relative to weekdays. There is no doubt that the reductions in ozone in the South Coast Air Basin (SoCAB) and other areas of California have been a great success. The question remains, however, whether these tremendous gains in air quality and associated decreases in air pollution related morbidity and mortality were achieved via the most cost-effective path. This point has not been addressed in a quantitative manner in the weekend effects report or comments, but it should be.

Professor Paulson makes a request that most people would love to see but is difficult to perform. Even identifying the most efficient route to achieving air quality standards would be difficult. For example, a VOC-only or a NO_x-only control strategy probably is not feasible in that the control measures for one precursor often affect the emissions of the other precursor. Also, a NO_x-only strategy might have some initial disbenefits but may arrive at the desired endpoint sooner than a dual precursor control approach. Any such quantitative analysis of the best route to healthful air quality would depend on modeling that "gets the right answer for the right reasons" and would also assume that the photochemical system remains "constant" as the controls influence the nature, distribution, and timing of emissions. As a prelude for modeling future impacts, it would be helpful to perform retrospective modeling analyses. In other words, can the photochemical models reasonably simulate the ozone trends that have been observed based on our current understanding of chemistry and the changes in emissions resulting from control measures enacted? If the models can reproduce the known past, then staff would have more confidence in the effects predicted for the future by modeling. Furthermore, successful (accurate) modeling simulations of the ozone weekend effect would increase confidence that the model is reasonably handling the important atmospheric processes and that the predicted impacts and relationships are trustworthy.

2.2. Carryover Aloft

The distinction between periodic and steady NO_x reductions is a focus of the debate over NO_x reductions. Relative to weekdays, weekend AM NO_x emissions are lower, VOC/NO_x ratios are higher, and O₃ levels are higher. If NO_x is reduced at all times and all places due to regulatory controls, will O₃ levels rise by a comparable amount as they do on weekends, or will the efficacy of VOC reductions be reduced due to concomitant NO_x reductions? The carryover aloft hypothesis may provide the mechanism for the difference between *periodic* and *steady* reductions of NO_x (e.g. SR xv). From the SR:

"This (carryover aloft) hypothesis assumes that large reservoirs of ozone and ozone-forming pollutants commonly persist overnight above the cool layer of air near the surface. On the following day, these pollutants are assumed to mix down to the surface as the surface is warmed by the sun. The pollutants that mix down from aloft are assumed to interact with fresh surface emissions in such a way that ozone measured at the surface on weekends is greater than ozone measured at the surface on weekdays."

The contribution of carryover aloft is likely substantial. Modeling studies and field data indicate that 20-35% of surface O₃ in the South Coast Air Basin can typically be

attributed to carryover aloft from the day before, or in some cases two or three days before ([Lu and Turco 1996], [Zhao and Hardesty 1999 and Zhang and Rao 1999] as cited in the SR, and section 2.5 in TSD based on SCOS data). The O₃ enhancement at the surface from carryover aloft arises from three physically distinct photochemical processes: 1) O₃ produced the day before is transported to the layer aloft and persists through the night; 2) O₃ is produced in the layer aloft during the current day, converting NO_y and reaching the "maximum O₃ potential" [Blanchard 2000, Blumenthal et al. 1997, Blanchard et al. 1999] and 3) precursors (primarily VOCs) stored aloft add to fresh emissions at the surface to enhance generation of surface O₃. The relative contribution of these three processes is difficult to quantify, but existing data indicate that mechanisms 1) and 2) are of the same order [Blanchard 2000] and are more important than 3). For example, Fujita et al. [2002b] determined there was a relatively small fraction of the hydrocarbons observed at Azusa during summer 2000 appeared to have been processed for longer than several hours. The contribution from (1) is moderated by O₃ loss due to reaction with NO, NO₂ and HO₂ and other species. Ozone concentrations aloft are frequently higher than O₃ at the surface, indicating that current day aloft production (2) is substantial (e.g., [Lu and Turco 1996], TSD 2.5, [Blanchard 2000]). O₃ production in the layer aloft is NO_x limited ([Blanchard 2000], TSD C-14) since this layer has typically been aged 18-24 hours from its first emissions (i.e., TSD 5.3-5). NO_x has a lifetime of less than 8 hours, much less than the organics. O₃ produced aloft will thus be highly sensitive to *absolute* NO_x emissions.

Staff concurs with Professor Paulson's comments. However, staff also has concerns about the assumption that air quality measurements at the surface (impacted by nearby and fresh emissions of pollutants) fully and accurately represent conditions and processes occurring above it. The atmospheric processes and resultant air quality in the air from several tens of meters to several hundreds of meters can strongly influence the surface air quality on a daily basis as the vertical mixing of air increases during the day and taps into its reservoir of pollutants.

The discussion in the SR regarding carryover aloft asserts that carryover happens every day, but has more influence on weekend days. The mechanism outlined in the SR asserts that on weekdays fresh emissions of NO_x quench O₃ from aloft, while on weekends the morning NO_x concentrations are low, so that the aloft O₃ makes a greater contribution. This mechanism is not implausible, however it would be more convincing if most mixing with air from aloft occurred in the early morning before NO is oxidized to NO₂. Mixing begins in the morning (SR) and has made a significant contribution by 10:00 [Lu and Turco 1996], but it continues into the afternoon (SR) as the mixed layer deepens, so that influence from layers aloft reaches a maximum in mid afternoon ([Lu and Turco 1996], TSD 2.5-5). Because the hypothesis presented in the SR emphasizes morning mixing of aloft layers, it also emphasizes O₃ generated via (1); carryover of aloft O₃ generated the day before. Further, given that O₃ is highest on Sundays in much of the basin, the carryover hypothesis in the SR suggests that O₃ on Mondays should be higher than other weekdays. However, the SoCAB 22 site average for 1996-1998 indicates that O₃ on Mondays is slightly lower than other weekdays. This is true for both high and medium O₃ days (Table 1.2-3, TSD).

Professor Paulson makes a valid point that has been raised by others challenging the plausibility of the Carryover Aloft hypothesis. People raising this point however are assuming that the surface O₃ measurements are representative of (and in fact the same as) the O₃ concentrations

aloft. Given that O₃ quenching is always occurring at the surface near ubiquitous NO sources (i.e., motor vehicles) and that conditions aloft are much more likely to be NO_x-limited with respect to O₃ formation, it should not be assumed (especially given additional layering tendencies for O₃ concentrations) that the surface O₃ measurements characterize O₃ conditions aloft. It is conceivable, given the lower NO_x emissions (at least during the morning), that the total amount of O₃ formed aloft and available for mixing down to the surface the next day is less on Saturday and even smaller on Sunday than on weekdays. If carryover is a significant factor in determining peak surface O₃ concentrations (25-30%), then surface O₃ concentrations on Monday could be the lowest of the week despite the large fresh emissions of O₃ precursors.

The following is proposed as an alternate hypothesis for the contribution of carryover aloft to day-of-week variability and to the dramatic reductions in O₃ exceedences over recent decades. Weekend O₃ levels are higher relative to weekdays due to a NO_x disbenefit, combined with a contribution from NO_x timing [Marr *et al.* 2002], and possibly a spatial shift in emissions between weekdays and weekends [Yarwood *et al.* 2002]. O₃ exceedences have decreased on weekdays due to combined VOC and NO_x reductions; the portion generated at the surface is somewhat VOC limited (see also Section 2.D.), while the aloft portion is NO_x limited. O₃ improvements on weekends have been more modest due to the so-called NO_x disbenefit, NO_x timing, and possibly a spatial shift in emissions. Reversing the NO_x disbenefit at the surface, however, is carryover aloft. Since production of O₃ aloft is NO_x limited, the contribution of carryover aloft has decreased over the past decades due to NO_x reductions. Lidar measurements of O₃ aloft during SCAQS in 1987 and SCOS97 analyzed by Roberts *et al.* [2001] are indicative of a significant drop in O₃ aloft between 1987 and 1997. The observation that O₃ is lower on Mondays than on other weekdays is consistent with NO_x limitation of O₃ aloft resulting in less carryover from Saturday to Sunday and from Sunday to Monday. It seems plausible that the contribution from O₃ due to carryover aloft has decreased more than same-day surface generated O₃, explaining some of the decreasing trend in O₃ exceedences over the recent years.

Staff concurs with this explanation.

Ozone exceedences in the early years (1964-1977), increased with day of week from Sunday to Friday; Saturday O₃ was between Sunday and Friday. This weekend/weekday pattern illustrates in inverse the more general effect of steady NO_x reductions as well as a generally NO_x-limited O₃ formation. Since traffic doesn't vary tremendously by day of week, the carryover effect explains the building trend in O₃ levels as the week progressed in past years. Significant carryover is also a possible explanation for some of the observed PM trends: Table 3.1-3 averages show substantial improvements in PM₁₀ nitrate between 88-91 and 97-99 all over the city on all days except W, Th, and Fri. This is consistent with the weekend effect coupled to the carryover reaching 2 days. If the mechanism by which carryover aloft proposed here is correct, then reductions in NO_x emissions in an absolute sense will directly reduce the substantial contribution of carryover.

Staff concurs.

2.3. The VOC/NO_x ratio

The SR, TSD, and much of the weekend effects research uses the VOC/NO_x ratio to determine VOC vs. NO_x limitation. Because of the spatial and temporal variability of the VOC/NO_x ratio and difficulty in measuring and interpreting it, discussed below, it is not an ideal indicator of VOC vs. NO_x limitation. The SR lists the VOC/NO_x TNMOC/sum of speciated VOCs ratio to average 4-9 in SoCAB, with the caveat that VOCs are likely underestimated and NO_x overestimated (SR 4-5). It uses an EKMA-based (box model) isopleth diagram to determine VOC or NO_x limitation; values below 8 are VOC limited, 8-10 limited equally by NO_x and VOCs, and above 10 by NO_x.

A central question to the weekend effect is the degree to which VOCs vs. NO_x are limiting O₃ formation at the surface in SoCAB and other parts of California. The VOC/NO_x ratio, and particularly the morning VOC/NO_x ratio, has traditionally been used as an indicator of VOC or NO_x limitation of O₃ formation. The VOC/NO_x ratio is an excellent indicator of the instantaneous production rate of O₃, however, state-of-the-art 3-dimensional models indicate that the VOC/NO_x ratio is a poor indicator of the limiting precursor for O₃ formation. This is because VOC/NO_x ratios diagnostic capability is clouded by several factors, including the fact that the VOC/NO_x ratio increases as air is aged, that pollutants are diluted above the surface in the mixed layer, that there is a contribution from NO_x-limited aged air carried over aloft and so forth ([*Sillman 1999*] and references therein). The emphasis on morning ratios arises from a traditional view of O₃ formation whereby downtown emissions are transported in relative isolation, producing high O₃ levels once they reach downwind areas. Blier and Winer's [1996] study on SoCAB indicated that transport is more limited, and that local and nearby emissions throughout the day have more responsibility in determining O₃ levels at a particular site. VOC/NO_x ratios are emphasized in the SR and TSD, and in some of the on-going weekend effects research, with a preferential emphasis on the morning VOC/NO_x ratios. VOC/NO_x ratios should be used with qualification, and afternoon ratios should be emphasized over the morning ratios.

Staff concurs.

2.3.1 Measurements of VOC/NO_x Ratios

CARB and DRI have devoted substantial effort to VOC/NO_x ratios. For VOCs, CARB relied on PAMS total hydrocarbon (THC) data, derived by integrating peaks (identified or not) and calculating their sum [*Main 2002*]. DRI used CO as a VOC surrogate based on correlations between measured CO and C₂-C₁₂ hydrocarbons + carbonyls [*Zielinska et al. 1999*].

- *Fujita et al.*[2000, 2002b] analyzed VOC/NO_x ratios in the late 1990s at 12 sites in SoCAB, and found that on weekday mornings, VOC/NO_x ratios averaged 6-10; on weekend mornings it averaged 7-14. At the daily O₃ peak in the afternoon, site average VOC/NO_x ratios were between 8 and 16 on weekdays and 9 and 18 on weekends. Azusa and LA N. Main were generally in the lower end of these ranges.
- CARB used 1997 PAMS 3-hour THC data for six sites in SoCAB (TSD 2.3). Late morning VOC/NO_x ratios were 4.3-7.7 on weekdays and 5.0-9.3 on weekends. The range is from 4 to over 30, raising the question if days that exceed the 1- and 8- hour ozone standards correspond to average or outlier

VOC/NO_x ratios. In models, high O₃ days have a slight tendency to be more associated with VOC limited conditions [Sillman 1999]. The CARB values are generally lower than those calculated by DRI [Fujita et al. 2000, 2002b], possibly because the DRI calculations are based on a more complete analysis of VOCs, one that includes hydrocarbons up to C₁₂ as well as aldehydes [Zeilinska et al., 1999].

- UCLA collected a limited set of data at Azusa on SCOS97 episode days [Paulson et al. 2002], and found (diurnally averaged) VOC/NO_x ratios of about 9 using the “sum of speciated VOCs” measurement, and about 13 for the TNMOC measurement. For comparison, the DRI calculated VOC/NO_x average ratios of ~7, 8, for weekday and weekend mornings, and 9 and 12 for weekday and weekend afternoons, respectively. CARB 1996-1998 values were about 6 on weekdays and 7 on weekends (TSD 2.3), with no discernable difference between morning and afternoon. Averages of UCLA measurements of VOC/NO_x ratios at UCLA, in West Los Angeles, during September and early October of 1999 and 2000 indicate strong NO_x limitation; average VOC/NO_x ratios are all above 16.

While this is by no means a definitive comparison, it does underscore the uncertainty of VOC/NO_x ratios, which are amplified due to the difficulty in measuring both VOCs and NO_x (below). Revising the references throughout the SR and TSD to VOC/NO_x ratios between 4 and 9 should be considered.

Staff acknowledges in the text that the calculated ratios likely underestimate reality by about 40% or more. Staff is hesitant to apply a crude corrective factor across the board to all measurements but will consider the suggestion as it is easy for readers just to take the numbers (without the associated caveats and notes) and “run” with them and thereby being led to potentially false conclusions.

2.3.2 Biases in VOC Measurements

Three research groups have recently published results that have attempted to address the question of how well PAMS and similar speciated VOC measurements report total VOC concentrations. All indicate that VOC loadings are substantially higher than the speciated measurements indicate.

TNMOC levels are higher than the sum of individually identified VOCs—PAMS THC or similar—for two reasons. One is material obscured in the baseline, likely dominated by individually small quantities of dozens of hydrocarbons, but with contributions from polar organics that tend to be smeared out by standard non-polar column phases. The second source of unquantified VOCs is compounds that are lost in the GC inlet, or that do not elute from the column during the course of one run. This material is likely polar or semi-volatile.

- At UCLA, Paulson and co-workers [Maris et al. 2003] have developed an instrument to measure TNMOC as a lumped total, after oxidizing the VOCs to CO₂. The TNMOC measurement attempts to both quantify material obscured in the baseline and the compounds that don't make it through the inlet or the column at all. The TNMOC sample is collected simultaneously with a sample that is analyzed with a standard GC column with a method similar to the

standard PAMS VOC analysis. Speciated chromatograms were analyzed by summing all detected peaks, so that material obscured in the baseline is not included in this measurement. TNMOC levels average 20-100% larger than the sum of the speciated VOCs measurement.¹ Average TNMOC/Sum of speciated VOCs ratios were 1.45 at Azusa during SCOS97, and 1.5 and 1.6 at UCLA on clear days during September - early October 1999 and 2000 respectively [Chung *et al.* 2003]. On cloudy days at UCLA during 2000, the average TNMOC/Sum of speciated VOCs ratio was 2.2, possibly due to increased influence of carryover aloft. At Burbank, a site with very high VOCs dominated by strong local sources, the TNMOC/sum of speciated VOCs averaged 1.2, similar to the value for gasoline vapor.

- Roberts *et al.* [1998] measured TNMOC/sum of speciated VOCs ratios of 1.2 – 1.4 in rural Nova Scotia with an approach similar to the one developed at UCLA.
- Alastair *et al.* [2000] used a 2-dimensional gas chromatographic technique to find dozens of undetected organics in the baseline of a speciated chromatogram, mostly containing 6 or more carbon atoms. Their TNMOC/Sum of Speciated VOCs ratios were ~1.7 in Melbourne, Australia. They attributed the extra material to the many hydrocarbons that are present at individually low concentrations, but which add up to a substantial amount of material. Their results underscore the uncertainty inherent in deriving THC or TNMOC from a measurement designed to quantify individual compounds. Because their measurement used a GC column, it may have missed many compounds that the UCLA instrument detects in its TNMOC channel.
- The Bendix 8202 TNMOC results suggest a factor of >2 higher VOC compared to speciated measurements, but these data are questioned in the TSD.

Clearly VOC loadings are substantially higher than PAMS and similar measurements indicate, but some portion of this isn't relevant to comparisons with models or the isopleth diagrams they generate. Isopleth diagrams have commonly been generated based on VOC/NO_x ratios in the emissions inventory or at the beginning of a chamber experiment. The portion of a TNMOC measurement due to oxidation products that form in a single day thus shouldn't necessarily be included in a VOC/NO_x ratio.

Theory predicts that oxidation products of same-day photochemical processing of fresh emissions should contribute a modest amount of material that a TNMOC measurement will detect but a speciated VOC analysis will miss. Chung *et al.* [2003] estimated the increase in oxygen or nitrogen content resulting from exposure to 0.1 ppt OH and 50 ppb O₃ for 4 hours. Under these conditions, an average of 30% of the hydrocarbons react once with either OH or ozone. Since the organics have an average of 7 carbons, and can be expected to add ~1.5 functional groups (primarily alcohol, carbonyl, or nitrate) per reaction, the total mix might increase its heteroatom content relative to the carbon content by about 7%. The effect of this modest increase on the TNMOC/Sum of Speciated VOC's ratio cannot be calculated precisely since the effect of

¹ These values are higher than those reported in Paulson *et al.* [2002]. The values reported here are based on a peak-based integration of the speciated VOCs chromatogram, rather than the baseline-based integration used in Paulson *et al.* [2002].

oxygenation/nitration can be to either reduce the FID response or to cause the compound to be lost or broadened in the column so as not to be quantifiable. The latter reduces the sum of speciated VOCs more than the former. It is clear, however, that given the small increase of heteroatoms expected from photochemical processing over the course of a day, that same-day oxidation products make a moderate contribution to the TNMOC/sum of VOCs ratio. This is borne out in the data; the ratio of TNMOC to sum of VOCs does not increase in the afternoon or correlate with O_3 .

The other material that makes up the difference between the TNMOC measurement and the sum of peaks is numerous individual hydrocarbons, directly emitted polar organics, or multifunctional oxidation products from carryover aloft. All of this material should be included in the VOC/ NO_x ratio.

VOC loadings are underestimated, by ~20 to 70%. NO_x measurements, as noted in the SR and TSD, tend to be overestimated due to the fact that NO_x instruments partially detect NO_z species as NO_x . The combination of these compounding errors is that VOC/ NO_x ratios are likely 20-60% higher than the PAMS analyses indicate, making most VOC/ NO_x ratios much less VOC limited than the 4-9 ratios indicated in the SR and TSD.

Staff concurs.

2.3.3 Indicators of VOC or NO_x Limitation

The weekend effect in and of itself, given the complex nature of changing emissions patterns, oxidants stored aloft and other differences, leaves much to be desired as an indicator of hydrocarbon vs. NO_x limited O_3 formation. The VOC/ NO_x ratio is an imperfect indicator of VOC vs. NO_x limitation as well. In addition to its uncertainties, temporal evolution and geographical shifts, VOCs and NO_x are precursors rather than a chemical signature of what has happened in an air mass. A number of compounds are formed preferentially under NO_x limited regimes, such as HNO_3 ; VOC-limited regimes produce compounds such as hydrogen peroxide preferentially. Sillman (1999) and others have explored the use of indicator ratios such as NO_y/NO_x and H_2O_2/NO_y [Milford et al. 1994; Chock et al. 1999; Winkler and Chock 2000; Sillman 2000; Sillman 1999], to trace the VOC vs. NO_x limitation history of air masses. The possibility of using a more robust indicator than the VOC/ NO_x ratio, mentioned briefly in the TSD (sect. 7), based on existing data or in future field measurements should be explored and elaborated on.

The routine data collection programs effectively limit the possible indicator ratios for analysis to VOC/ NO_x .

2.4. Emphasis on Average Values Rather than High Ozone Days

O_3 formation is well known have a nonlinear dependence on NO_x and VOCs, and on the ratio of the two. Because of this, analyses based on averages rather than design days can be biased (e.g., MacGregor and Westberg [1990]). Several additional examples are as follows:

- Section 1.2 of the TSD offers an analysis of O_3 levels binned into high, medium and low O_3 days. While the medium and high O_3 days track one

another reasonably well during 1996-1998, the low O₃ days have quite different behavior by day of week.

- During 1992-1994, the high O₃ days were most dissimilar from the other two groups.
- As cited on page 1-11 of the SR, the 1-hr max has gone down faster than has the top 30 average.

Averages are used widely in the TSD as well in much of the weekend effects Working Group research (e.g., *Fujita et al. [2002b]*). Many of the analyses would be more convincing if events leading to O₃ above the design values were analyzed separately from low O₃ days.

Staff will consider the feasibility of focusing on high O₃ days in future analyses.

2.5. Isopleth diagrams

ARB Staff rightfully points out in several places in the SR and TSD that isopleth diagrams shift depending on the geographical location they represent and numerous other factors. This point is overshadowed by the apparent simplicity of the relationship between VOCs, NO_x and O₃ implied by the single isopleth diagram in the SR. Given the importance of the isopleth diagram(s) to the debate over the causes of the weekend effect, this diagram(s) should be carefully chosen. Output from a state-of-the-art grid model that accurately represents carryover aloft as well as boundary effects, mixing, and so forth would be preferred over the diagram presented. This isopleth diagram is based on precursor concentrations that are several years out of date, so it is not surprising that the weekend effect does not appear to be predicted by the isopleth diagram in the SR & TSD; reductions on weekends of ~20% ROG and ~40% NO_x relative to weekdays from the upper right hand corner don't result in higher O₃. This diagram should be replaced by one that is more representative of the current conditions in SoCAB, or elsewhere in California.

There are several ways to address this issue. One is to use a simple box model without additional emissions to generate the simplest form of an isopleth diagram, and discuss how this can (and can't) be used to discuss O₃ formation at different locations, times, etc. An alternative is to use a state-of-the-art airshed model and consider plotting the number of grid cells in the modeling domain that exceed a particular O₃ levels (i.e., *Chock et al. [1999]*). This avoids the problem that isopleth diagrams at different locations have very different shapes (e.g., *Wang and Milford [2001]*).

Staff has included a more pertinent EKMA diagram but will not generate new ones.

2.6. The NO_x Disbenefit

There are several lines of evidence pointing to a significant NO_x disbenefit in the SR, TSD, appendices and on-going research. The disbenefit is also illustrated in the following plot, based on data presented in the TSD:

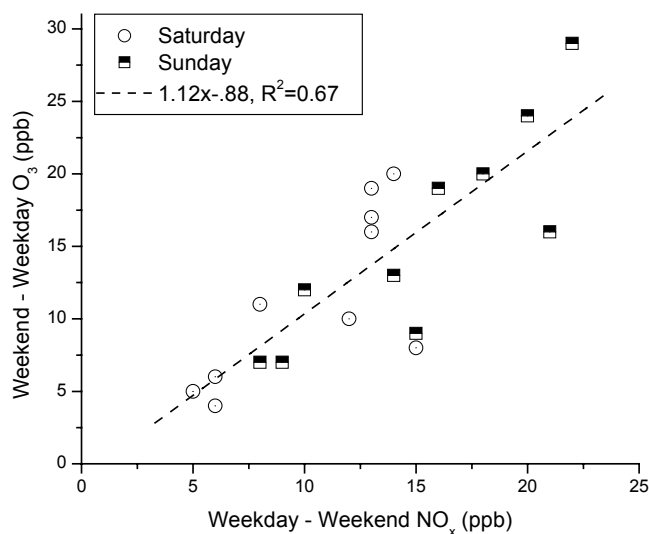


Figure 1. The relationship between average maximum O₃ levels and the NO_x concentration at the O₃ peak for 10 sites in SoCAB: Anaheim, Azusa, Burbank, Hawthorne, LA - N. Main, Lynwood, Long Beach, Pico Rivera, Pomona, and Reseda, based on data presented in section 5.3 of the TSD. The low outliers at 15 ppb NO_x are Lynwood data.

The Figure shows a strong anti-correlation between the ozone and NO_x in the afternoon at the ozone maximum. While the concentration of NO₂ is greater than NO at this point, NO concentrations are not zero in the averaged data. There is no correlation with local morning weekday-weekend NO_x differences at each site ($R^2 < 0.01$), and a weak correlation with afternoon CO differences ($R^2 = 0.18$).

Staff was initially confused until noted that Y-axis featured WE minus WD while the X-axis featured WD minus WE. Staff acknowledges the anti-correlation between O₃ and NO_x at the time of peak O₃ and the lack of correlation of between weekday and weekend peak O₃ with morning NO_x. Part of this association may also be due to O₃ quenching.

2.7. Spatial Shift in NO_x Emissions

The on-going model-based research by Environ [Yarwood *et al.* 2002] supports a contribution of the shift in spatial distribution of emissions, particularly NO_x, as contributing to the weekend effect. This hypothesis has significant merit, and might produce a contribution of the same order as NO_x timing. Why is a geographical shift in emissions not considered as one of the primary hypotheses for the cause of the weekend effect?

Staff did not list the spatial shift as a separate hypothesis because the limited data and potential analyses would prevent the inclusion of substantial detail. Staff did include spatial shifts in activity when discussing the complexity of the weekend effect. Staff will include an evaluation of the impact of spatial shifts from weekday to weekend in emission activities in the recommendations for modeling.

Specific Comments for Each Section of the SR

Note: Comments are listed by page, Figure or Table number in the Draft Executive Summary and Staff Report. P indicates the paragraph number on the indicated page, exclusive of headings.

xiv It should be noted that average ground level HC/NO_x ratios *average* less than 8-10. The reports would be improved with analysis HC/NO_x ratios on high ozone days and periods of rapid O₃ production. If this is not possible, the text should indicate that the average might not accurately predict hydrocarbon vs. NO_x limitation.

Staff noted the subjectivity and uncertainty.

xvi Carry Over aloft hypothesis: See carryover aloft section 2.B above for an alternative hypothesis regarding the role of carryover aloft in the weekend effect.

Staff redrafted.

2-3 last P Same comment as for xiv. Additionally, an indication of the historical trend would be very helpful. If that were not possible, data for a few points in the past (e.g., SCAQS, etc) would be very helpful to the discussion.

Staff provided although subject to limitations.

2-7 P3 The comment about the independence of the NO_x timing effect is not clear. Most likely the NO_x timing effect isn't independent of the other factors. Was it meant to point out that NO_x timing likely isn't independent thus we can't actually observe the indicated predicted outcomes? This paragraph presents some subtle points that would be better conveyed with more explanation.

Yes. Staff has expanded discussion.

2-9 P. 2, and 2-11 P 4. The comment regarding radicals warrants more explanation. Most radicals do not survive long enough to be carried over aloft, although some peroxy radicals that are freshly generated aloft are presumably mixed down.

Staff rewrote. Although radicals likely do not have significant carryover, radical precursors (e.g., O₃, HCHO) can have significant carryover.

2-10 P2 This paragraph needs clarification. It should be expanded to lay out the expected difference between this effect on weekends and weekdays. As written, this paragraph also seems to be contradictory to P4 on this page.

Staff has expanded discussion.

3-7 Finding 11, isopleth diagram: The SR leads the reader to believe that much of the area affected by the weekend effect are more strongly NO_x limited than the data support. It also overstates the certainty with which VOC vs. NO_x limitation is known. It is

overly-focused on the early morning VOC/NO_x ratios, to the exclusion of the contribution of photochemistry during the O₃ production period later in the day, and in layers stored aloft.

Staff did not understand the reference to the isopleth diagram but rewrote to better portray the uncertainties.

3-8 P 1 This statement implies a causality that seems incorrect. NO₂ concentrations don't decline independently of the NO levels unless the NO₂ comes from carryover. Most of the NO₂ likely does not come from carryover. The NO₂/NO ratio is higher because there is a higher level of photochemical activity, consistent with the NO_x-disbenefit, NO_x timing, and carryover aloft hypotheses.

Not necessarily incorrect but staff rewrote for more clarity.

3-8 P 6 Does VOC reactivity decrease significantly as air is aged on the time-scales relevant to air pollution events (~36 hours)? Likely somewhat, but less so than indicated by conventional hydrocarbon analysis, since so many of the oxidation products are more reactive than their parent hydrocarbons, and go undetected.

Staff concurs and rewrote.

3-9 Finding 14 Point 1: This important point would be better communicated if the improvements were presented quantitatively.

Staff enhanced point.

3-10 A comment regarding the results for a difference in spatial distribution of emissions between weekends and weekdays should be added. Consideration should be given to adding a geographical shift in emissions on weekends as an additional weekend effect hypothesis.

Staff has considered. Staff did not incorporate in this report but recommended for future efforts.

4-2 P 5 In addition to NO_x emissions contributing inevitably to NO₂, PAN and PM nitrate, they also must contribute to toxic nitro-PAHs, to nitrogen fertilization, and to the regional increase in background O₃. This background O₃ is sufficiently elevated to make meeting the 8-hour 80 ppb standard difficult in many areas of California and the region. Anthropogenic activities in the State of California make a non-negligible contribution to this highly NO_x-limited phenomenon.

Staff has expanded discussion.

4-5 2nd to last P These statements are unclear. The term "low NO_x" is generally used for NO_x limited conditions where peroxy radicals react with one another rather than NO and nitric acid formation is limited; its unlikely that 60 ppb NO_x defines the transition to "low NO_x" chemistry for many of the ambient conditions under consideration. Is this paragraph indicating that the VOC/NO_x ratio has brought the air into NO_x limitation?

Staff rewrote.

5-2 P 2 States: "For at least 15 weekday-weekend transitions ...during the ozone seasons, hourly surface measurements would include HONO, nitrate radical and PAN." There are many specialized measurements that could provide useful insights into the weekend effect and the question of VOC or NO_x limitation, including several aimed at organics, and at "indicator" species such as nitric acid and hydrogen peroxide. Why was that particular set of NO_y species targeted?

Staff has expanded the list of targeted species.

5-7 P3 This is a subtle concept that deserves some further explanation. It seems a bit misleading since the NO_x timing effects that we may or may not observe are not decoupled from concentration reductions.

Staff expanded.

Specific Comments for the Technical Support Document

Note: Comments are listed by page, figure or Table number in the Draft TSD. P indicates the paragraph number on that page, exclusive of headings.

1.1-1 P4 L 4 While the robustness of the 2nd to 11th highest days as an indicator seems intuitive, is there a stronger justification that could be added?

Staff has provided reference.

1.4-11 Why were sites such as Banning not included in this analysis?

Site location changes between periods would bias results.

2.4-2 (Ozone precursors): point 3; Weekend/weekday reactivity differences increase in the afternoon - i.e., reactivities are lower on weekend than weekday afternoons. This is counter intuitive since there is a relatively larger contribution from fresh emissions in the afternoon since there are rather lower emissions on weekend mornings. Perhaps this is partly due to carryover aloft. If so, carryover likely brings more unmeasured emissions, partly compensating the decreased reactivity in hydrocarbons with unmeasured polar and other oxidation products.

Staff has addressed.

2.4-2 P5, Aged air aloft may also contribute to the apparent lower reactivity of organics in the afternoon relative to the morning. However, both same-day and especially aloft photochemically processes air likely contains significant under-reported and unreported organics, so the difference in reactivity may be small.

Staff rewrote.

2.5-3 and 2.5-4 First, the usefulness of the Arco tower analysis, based on the comparison of an O₃ monitor at 100 m with another at ground level ~ 1 mile away from the base of the tower isn't clear. Local variations, or more importantly, the absence of local variations, between the two sites have not been established. Further, 100 m only represents the lowest 20% or so of the mixed layer that forms in a typical diurnal cycle. Next, although perfectly reasonable efforts were made to correct the data, the ARB audit team invalidated the instrument. The author feels that Section 2.5.4.1 (not 2.5.4.2) discussing the Arco tower data should be cut unless the following can be established: a) it can be shown that O₃ levels at the base of the tower are the same as the site used for comparison 1 mile away, and b) sufficient data for statistical significance in the analyses can be shown.

If Staff decides to keep the section, there are several points in need of clarification:

Comparison of day-to-day O₃ concentrations between the surface site and the tower: Indicate and justify the criteria for correlation/non-correlation of the O₃ data.

Staff has deleted section.

2.5-4 P3 Clarify: "Decreases in ground level ozone concentrations showed influence of carryover manifested in either ozone aloft profiles not changing at all from day to day or changing significantly."

Staff has deleted section.

2.5-3 P2 Clarify: "Carryover generally depends on continuation...", and so forth.

Staff has deleted section.

2.5-3 P 3 Is the reverse true—i.e., do high correlations indicate high O₃ aloft? The Tables in this section need more explanation.

Staff has deleted section.

3.1-12-14 Why is there no discussion of the improvements over the 1988-1999 period in this summary section?

Staff has included.

3.1-15 or elsewhere: It is useful to point out that PM nitrate is much less responsive to VOC controls when O₃ formation is VOC limited than it is to NO_x controls when air is NO_x limited (e.g., *Harley et al. [1997]*).

Staff has included.

Section 4. It might be instructive to explore other hazardous air pollutants (HAPs). NO_x plays a central role in generating HAPs, such as nitro-PAHs (e.g., *Finlayson-Pitts and Pitts [2000]*; *Phousongphouang [2000]*).

Staff did not include but will recommend suggestion for future work.

5.3-1 This analysis would also benefit from hourly VOC data. The results would be more convincing were it not necessary to use CO as a VOC surrogate.

Staff will not include hourly VOC data as high quality data are not available. The reader will be referred to Figure 2.1-29 (diurnal plot of CO) and Figure 2.1-89 (diurnal plots of Total Hydrocarbon concentrations) for an indicator of the similarity in CO and THC (VOC) and what the general diurnal profiles for VOCs might look like.

5.3-1 P2 The relationship between VOCs and CO for light duty vs. heavy-duty vehicles should be added here.

Staff has included.

5.3-1 P5 Why was the time interval midnight to 4 PM chosen?

Staff has elaborated.

6.1-4 Section 6.1 is a particularly well-written section of the TSD. A minor point: the reference in P1 of this page to VOC/NO_x ratios with 2 significant digits implies a much higher degree of certainty in the VOC/NO_x ratios, as well as more uniform values, than is justified.

Staff did not change despite large uncertainty as the "false precision" is used to illustrate the modeling sensitivity to small variations in a crude measurement.

Section 7 presents an excellent preliminary research plan for the weekend effect.

7.1-3 This introduces for the first time in the TSD the concept that the weekend effect has a seasonal component. This interesting clue should be expanded upon elsewhere in the TSD, and, if appropriate, in the SR.

Staff has rephrased.

7.1-7 P1, 7.1-8 P1 This section makes several mentions of the potential value of "indicators" of hydrocarbon vs. NO_x limitation. These are not mentioned, much less analyzed anywhere else in the SR or TSD. This topic should be addressed both in the TSD and SR; see also 2.C.3 above.

Fair amount of discussion already; staff considered expanding but the amount of data for "other" indicators is very limited.

7.1-15 This section implies a partially independent effect from low NO_x concentrations relative to high VOC/NO_x ratios at high NO_x concentrations. This important point should be developed elsewhere in the report(s).

Staff primarily wanted to ensure that the chemical mechanisms are validated for the current range of conditions that are observed at ground level and aloft.

8. The modeling section does a good job of addressing the points it sets out. Particularly, the author whole-heartedly supports the underscoring of significant uncertainties regarding low NO_x chemistry, and the influence of layers aloft, as well as the more routine but very critical uncertainties in boundary conditions and emissions.

No comment needed.

Appendix A: In contrast to the data presented in this section, Chock et al. (1999) results indicate that the NO_x disbenefit is much weaker for the 8 hour standard than it is for the 1 hour standard. Sillman (1999) also cites modeling results showing that lower precursor concentrations and lower peak O₃ values tend to be associated with a weaker VOC limitation, even given the same initial VOC/NO_x ratio.

Staff has included Chock reference in the staff's response.

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Weekend Effects Peer Review Editorial Comments

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Staff addressed all editorial comments.

A. Staff Report

- 1-7 last P lines 3-4 is there a typo here? It's not so clear what is meant but it seems counter-intuitive.
- 2-3 last P It would be useful to state what the weekend VOC/NO_x ratios are, rather than reporting them relative to the weekday values.
- 2-5 P 3 11 AM not PM
- 2-8 Theory section—several blank lines; why?
- 2-9 Line 2 “see” what?
- 2-15 The citation for this diagram and its repeat in the TSD is incorrect—the diagram in Finlayson-Pitts and Pitts [*Finlayson-Pitts and Pitts 2000*] is substantially different than that in the SR and TSD.
- 3-6, 3-7 The averaging for the VOC/NO_x ratios should be indicated. Is this for the high O₃ days?
- 4-2 P 5 What is meant by “relatively recently?” in regards to achievement of the NO₂ standard?
- 5-4 P5 “including” (typo)

B. Technical Support Document

- 1.1-1 P5 L 1 For clarity, means of what?
- 1.1-2 Table & related text: What does 80/82 and 96/98 mean? Averaged results for 80, 81 and 82, etc., or something else?
- 1.2-1 This section should specify how the confidence intervals were computed.
- Sect. 2.5.4.1 Referring to the point measurement on the ARCO Tower as an “ozone profile” is confusing and should be changed.
- 2.5-5 P2 Last lines imply (unintentionally, I believe) that no additional chemistry occurs in the layers aloft.
- 2.5-13-18 What do the circles represent?
- 2.5-8 Table 2.5-1 are these 1 hour or 24 hour averaged O₃?
- 2.5-8 Table 2.5-2 Same question as above, and why doesn't Table 2 average to Table 1? It seems preferable to expand the titles for these Tables or to add notes so that the reader can consider these tables independently and draw some conclusion from them. A minor part of the problem is that the lightly and darkly shaded areas are not differentiable in black and white. Further, the high correlation shaded areas in Table 2 are fairly randomly distributed.
- 3.1-14 P3 line 1 “understanding” not “understudying”?
- 3.1-14 P5 VOC uncertainties, while valid, seem to be overemphasized here.

3.1-15 P2 "scattering" typo

Figure 5.1-1 This figure is not readable.

5.1-28 to 42 Plots. It is very difficult to differentiate the day of week in black and white.

5.3-1 From reading, the numbers listed in P2 appear to be averaged over the whole week—this isn't made clear. Judging from the fact that the multiplication of the numbers in P3 and P3 are result in those in P6, however, it appears that the numbers in P2 are instead mid-week numbers, which they should be. The mid-week averages provide for direct comparison with the reductions in vehicular traffic and the resulting reductions in ambient CO and NO_x. If the numbers for relative contribution to NO_x and CO emissions in P2 are full week averages, then the values quoted in P6 will be off to a degree.

This simple calculation using WIM data results in remarkable agreement between the concentration data and that expected based on the day-of-week variation in vehicular traffic on Sunday. The reductions in vehicular traffic for Saturday would seem to indicate a somewhat larger reduction in CO and NO_x concentrations than are observed.

Table 5.3-2 Add a note indicating that VOCs change less (presumably) than its surrogate listed in this Table, CO.

Table 5.3-3 Add units.

Figures 5.3-1 and -2 These Figures would be better presented in mass units, or with Tables along side that present mass units. The presentation of percents over-emphasizes changes when NO_x and CO values are at low concentrations and don't contribute as much to secondary pollution formation.

Mass units were presented in Chapter 2. The percentages are useful here for comparing activity with air quality.

Figure 5.3-3 Indicate in the figure legend how the VOC/NO_x ratio was calculated.

7.1-3 P4, last line, I suggests adding ", such as VOCs," between "pollutants" and "must".

7.1-4 P5, 7.1-9 P2 and 6, the number of days recommended for aloft sampling is not consistent.

7.1-5 P3 What is meant by "discriminating" sites?

9.1-9 20 should be by Winner not Winer

PEER REVIEW of the ARB Staff Report: The Ozone Weekend Effect in California

Report to the
California Air Resources Board
Interagency Agreement No. 98-004, Task Order 12

November 27, 2001

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Summary

The motivation of the report appears to be a response to objections to NO_x controls based on the premise that weekend ambient O₃ levels are higher on weekdays, and that this is a result of a disbenefit from NO_x emissions controls. Further, the claim appears to have been made that the O₃ weekend effects is evidence that NO_x controls are counter productive for reducing O₃, and that new NO_x reductions should not be implemented. The staff report attempts to respond to these claims by providing a comprehensive review of the science issues associated with elevated weekend O₃ concentrations.

In particular, the staff report reviews existing data that might support or refute 5 alternative explanations (hypotheses) for elevated weekend O₃. These include the following:

1. NO_x inhibition of O₃ production on weekdays in conjunction with lower NO_x emissions and O₃ increases on weekends.
2. More even temporal distribution of NO_x emissions on weekends so that more O₃ is produced per molecule of NO_x (i.e., higher O₃ production efficiency per NO_x).
3. Increased carry over at the surface of O₃ and precursors on Friday and Saturday nights.
4. Increased carry over aloft of O₃ and precursors on Friday and Saturday nights.
5. Increased weekend emissions of precursors VOC and NO_x.
6. Decreased soot and increased actinic flux on weekends.

Staff concludes that hypotheses 3 and 5 do not play a role in the weekend effect, but that hypotheses 1, 2, 4 and 6 may each have some effect in increasing weekend O₃. Moreover, staff concludes that additional research is needed to determine the possible contribution of each of these explanations to weekend O₃.

Based on a review of the staff report and supporting documents, it appears that the staff findings are substantially correct. However, there are three major areas in which the report can be improved:

- Revisions are required to improve the organization and clarity of the report.
- A more complete summary of VOC-NO_x-O₃ photochemistry should be presented in a background section, and the explanation of the hypotheses should be refined.
- It may be possible with the existing data to rank the remaining four hypotheses in terms of the probability that they contribute to weekend O₃, and this ranking can be used to prioritize future research. In particular, the currently available

evidence suggests that hypotheses 1 and 2 are most likely play a dominant role.

The staff recommendations for future research are comprehensive and address most of the key issues. However, serious consideration should be given to the cost and the potential benefit of carrying out a major, new, intensive field study. The nature of the weekend effect is such that long term modeling of key indicator species at many sites throughout CA would be more useful than an intensive field study. Future laboratory research and ambient monitoring should especially target those species and processes related to the radical budget which determines the sensitivity of O₃ to VOC and NO_x and O₃ production efficiency per NO_x which are most likely the key contributor to the weekend effect.

General comments:

As stated in the report, the motivation for weekend effect studies is the claim by some members of the public that NO_x emissions reductions for the purpose of ozone control should be abandoned. The report correctly states that NO_x controls have been effective for achieving large reductions in ozone during the last 30 years, and furthermore, NO_x emissions are an essential component of control strategies for several other pollutants, including fine particulates, toxics, and regional haze. NO_x reductions also result in important benefits for reducing regional ozone, reducing acid deposition and nitrate deposition. Nitrate deposition can cause fertilization and eutrophication of surface waters and soils, possibly leading to promotion of invasive species, ecosystem changes and loss of endangered species. Because of the wide range of effects of NO_x emissions it is unlikely that NO_x controls would be abandoned.

Moreover, the NO_x disbenefit effect, whereby NO_x reductions cause increased O₃, will occur only for relatively small NO_x reductions at low VOC/NO_x ratios. If large NO_x reductions can be obtained such that the ambient VOC/NO_x ratio is increased, new NO_x reductions will then produce substantial benefits for reducing ozone. For example, as NO_x controls are phased in over a period of time, new NO_x controls may initially produce a disbenefit but will ultimately provide a much larger benefit. This raises an important flaw in the argument that NO_x controls are counter productive. Even if the NO_x reduction hypothesis is found to be the major cause of the weekend effect, this does not necessarily mean that NO_x controls would or should be abandoned. Yet in several instances the staff report seems to implicitly accept that a finding of a NO_x disbenefit would mean NO_x controls are ultimately counter productive. The authors should be careful to avoid linking a finding of a NO_x disbenefit to a conclusion that NO_x controls should be abandoned.

In light of these observations, the report should more thoroughly document the benefits of NO_x controls. The report could also address the possibility of a short term disbenefit combined with a long term benefit from NO_x reductions. While a quantitative analysis of the disbenefits versus benefits cannot be performed in the scope of the staff report, it would be useful to layout a strategy for contrasting and comparing a possible short term disbenefit versus a long term benefit (most likely using modeling studies). Finally, day of week variability in precursor emissions presents a fortuitous experiment in precursor modulation and is an important research opportunity for testing and improving the

reliability of photochemical models. The report should emphasize this opportunity and provide an outline of how the proposed research on the weekend effect can effect better predictions of the magnitude of additional precursor reductions (VOC and NO_x controls) necessary for attaining air quality standards for urban O₃

The report should present a more comprehensive background section on air pollution chemistry, especially as it relates to O₃ sensitivity to VOC and NO_x (see detailed comments below).

All section, sub-section and sub-sub-section headings should be numbered. This will facilitate referencing and navigating the report and will better demark transitions in topics. It might also be useful to use numbers or letter to bullet the "Questions" in the Executive Summary, and the "finding", etc. throughout the report for ease of reference.

The "question and answer" format works well for a non-technical audience. ARB should consider whether two documents are needed - one designed for a non-technical audience and one designed for a technical/scientific audience. If a single report is used, it might be appropriate to move more detailed sections on air pollution chemistry to appendices.

The scientific issues raised in the report are sufficiently complex that ARB should consider inviting additional participation from the academic/research community in the form of subsequent technical reports and/or a standing scientific review committee.

It appears that some of the chapters may have been written by separate teams, and there is some duplication of material between sections or chapters. For example, both chapter 1 and 2 contain background information on atmospheric chemistry, but neither section addresses it adequately. All listings of chemical reactions should be numbered, and they should be moved to a comprehensive chemistry section in the background.

Staff notes the general comments and has incorporated the suggestions and approaches as feasible. Most of staff's efforts have focused on the Staff Report because it is more likely to be read. For instance, a new Chapter 2 is being included to provide more atmospheric chemistry background and a common reference point for the discussions of the chemical aspects of the various hypotheses.

Specific Comments

comments on "Abstract":

The abstract should also describe the opportunity that is presented by the weekend effect for increasing knowledge about air pollution chemistry and for better determining the magnitudes of precursor reductions needed for attaining air quality goals.

The changes associated with the weekend effect does present an excellent opportunity for learning more about atmospheric processes and for evaluating the comprehensiveness of air quality models and the ability to accurately respond to perturbations in emissions.

Further examination is required of the staff recommendation that VOC controls should outpace NO_x controls. Staff should evaluate whether it is possible to achieve sufficient NO_x controls such that the South Coast Air Basin (SoCAB) becomes NO_x limited. While such a scenario may be unlikely due to large NO_x emissions from mobile source, staff should consider the long term prospects for NO_x reduction from alternative vehicles, and should identify at what point in time a primarily NO_x control strategy could become feasible. For VOC controls, staff should also consider reactivity based controls. In particular, because the SoCAB is radical limited, staff should consider the potential benefits of selective controls of radical sources such as carbonyls and aromatic VOC.

The initial staff recommendation that future VOC controls should outpace NO_x controls was based on the available evidence that VOC emissions have been reduced at least 50% more than NO_x emissions and that ozone formation in the surface layer of the SoCAB is likely VOC-limited. If the apparent NO_x disbenefit effect associated with the weekend effect is representative of what would happen with NO_x controls as some claim, then it is likely that a greater rate of NO_x control than VOC control would cause/permit ozone to increase until the ozone formation "ridgeline" were to be crossed. As Professor Tonnesen notes, additional work is needed to determine the magnitude of such a temporary disbenefit and whether the ultimate endpoint with NO_x reduction would yield more health and welfare benefits than maintaining the current control program.

comments on "Executive Summary"

"How big is the ozone weekend effect":

It would be informative under this topic to list at how many sites and how frequently the weekend effect results in exceedences of the state and federal O₃ standards.

Because exceedances are counts above a threshold, it is difficult to generically say how many exceedances the weekend effect causes as it depends on the frequency distribution of the daily maximum 1-hour concentration. The percent change in the mean concentrations from weekday to weekend are easier to determine; however, the lower mean concentrations in the western half of the SoCAB result in larger percentage increased there relative to the eastern basin. The number of standard exceedances in the western portion of the basin is much lower than in the central basin which is lower than in the eastern basin. The size of the weekend effect is dependent on the statistic used to characterize it. Some people like to emphasize the largest percent increase despite the fact that the ambient concentrations at such sites are low and exceedances of the health-based standards are rare. The weekend effect is still obvious when exceedances are used as the characterizing statistic. The effect tends to be stronger with the national standard than with the lower State standard. The effect is least noticeable in the western basin where few exceedances occur, is greatest in the central and eastern basin, but becomes less noticeable at the eastern extreme of the basin, particularly for exceedances of the State standard.

Page xiv, "Why do some believe the ..."

The answer to this question describes the NO_x reduction hypothesis as the theory that

NO_x reductions will be counter-productive for controlling O₃. There are actually two separate theories encompassed within the "NO_x reduction hypothesis".

- A. NO_x reduction can at times result in increased concentrations of O₃.
- B. NO_x reductions are counter productive for attaining air quality standards for O₃.

It is possible that A be true and at the same time B is not true. For example, it is possible that NO_x reductions may cause some transitional increases in O₃ as we make progress toward attainment of O₃ standards, but that NO_x reductions will be essential for ultimately attaining the air quality standard. It is critically important that a distinction be made between these two different hypotheses because an affirmative finding of hypotheses A does not imply that additional NO_x controls should be abandoned. The staff report, however, can be easily interpreted to frame A and B as a single hypothesis such that an affirmative finding of A would imply that future NO_x controls should be abandoned. Even if A is affirmed (which seems likely) a substantial amount of additional study is necessary to determine whether B is true.

Staff agrees that NO_x reduction may produce some variable amounts of disbenefit in peak O₃ concentrations in areas where O₃ formation is VOC-limited. Staff agrees that A does not necessarily lead to B.

page xvi, "Are there other possible causes of..."

The 3rd sentence in response contains the statement "Contrary to the NO_x reduction hypothesis, the alternative hypotheses do not imply that NO_x reductions would be counter-productive for reducing O₃." This raises the same issues as the previous question, i.e., that an affirmation of the NO_x reduction hypothesis implies that further NO_x controls are counter-productive. In fact, it is possible that NO_x reduction may cause transitional O₃ increases while still being the most effective means to achieve O₃ air quality goals in the longer term.

Staff attempted to reword material such that the context of the NO_x disbenefit is noted (e.g., VOC-limited locations and times of day) and that the impact of NO_x reductions could be short-term and variable.

In the summary of the "Carryover aloft hypothesis" it should be stated explicitly that this hypothesis is that there is an accumulation during the weekdays and greater carryover aloft of O₃ and/or precursors on Friday and Saturday night.

High O₃ concentrations tend not to develop from one day to the next but tend to build up over a period of days as the atmosphere becomes more stable. This seems to be true in the surface layer and may likely be true in the air aloft. Staff incorporated such information in the paragraph. However, the increased emissions of O₃ precursors during Friday and Saturday evenings tend to be into stable air near the surface (marine or radiation inversion) and might not mix up to the polluted air aloft.

Page xvii, last paragraph

This is an important observation and is well stated. It would be useful to add another two sentences stating: "As a result of these weekend timing effects, the O3 response to lower NOx emissions on the weekend may not accurately predict the O3 response to additional NOx reductions on weekdays. This could imply that the lower NOx emissions can cause increased O3 on weekends and reduced O3 on weekdays due to the timing of the emissions."

Staff incorporated suggested sentences.

Page xviii, 4th paragraph beginning "Low NOx emissions on..."

This hypothesis is incorrectly described such that it essentially repeats hypothesis number 1. The carryover aloft hypothesis, when properly formulated, is that more O3 and/or more precursors are carried over aloft on Friday and Saturday night. Another way of describing this is that there is accumulation of O3 and precursors during the week, and high weekend O3 results from the buildup on weekdays. Moreover, lower O3 levels on Monday/Tuesday could reflect the reduced precursor emissions on the weekend. (see more detailed comments on this below).

Staff believes this paragraph is essentially correct and that the atmospheric processes do not indicate substantial carryover, either at the surface or aloft, of emissions associated with greater activity on Friday and Saturday evenings. It may very well be, however, that the dynamics of the ozone system, interacting at the surface and aloft, results in a net lag of a day or two in creating the peak or minimum O₃ concentrations.

Page xx, 2nd paragraph beginning "Measurements of VOCs (ppbC) are needed...."

The units ppb or ppbC are not needed here – VOC can be measured and converted to any appropriate units, and it is distracting to specify ppbC measurements. However, later in the report when VOC/NOx ratios are described, it is essential that the unit be given either as ppm/ppmC or ppb/ppbC. This is because the value of the VOC/NOx ratio will depend on whether ppm or ppmC units are used.

Staff has done.

Page xx. bullet on "Laboratory experiments"

The report should state specifically the need for laboratory studies on the sources and fate of free radicals because the radical budget is critical for determining the response of O3 to changes in VOC and NOx at low VOC/NOx ratios. See additional description of this below.

Staff has done.

Page 1-2, 2nd paragraph, 3rd sentence beginning "Federal and state standards ..."

"concentrations as low as 95 and 125 ppb" should be replaced with "90 and 120 ppb". Although policy decisions have resulted in the standards being enforced at the 95 and 125 ppb levels, the health effect findings and the air quality standards specify 90 and 120 ppb. For example, the next sentence in the report correctly describes the regional standard as 80 ppb.

Staff has done.

Page 1-2, 4th paragraph, 3rd sentence beginning "The importance ..."

This paragraph is confusing and is incorrect as stated, e.g., in the radical limited regimes such as the SoCAB, O₃ formation is strongly correlated with VOC. Better just to delete this paragraph.

Staff provided additional references supporting that, on a global scale, the amount of ozone in the lower troposphere is directly and positively related to the amount of NO_x present.

Page 1-2, 5th paragraph, beginning "The relationship..."

More detail is required here on the chemical reaction mechanisms that cause O₃ to be inhibited. This paragraph should also state that O₃ sensitivity to VOC and NO_x can vary depending on the time of day - reference Tonnesen and Dennis, 2000a.

The Introduction section of the Staff Report is not the best place to go into more chemical detail. Staff has included a new Photochemistry Background chapter (Chapter 2) to provide more detailed chemistry and a centralized reference point when the chemical reactions associated with the discussion of various hypotheses is discussed later. Staff has included a sentence to highlight the time of day dependency.

Page 1-3, bullets at mid page:

The bullet "No other major pollutant behaves like ozone" should be rephrased: "No other major pollutant exhibits a weekend effect as does ozone."

Staff has done.

Page 1-4, Last paragraph:

This paragraph is somewhat confusing - does it imply that only VOC controls are being used in central/northern CA? Are there any other NO_x controls apart from the statewide

vehicle program?

No. The SCAQMD has been most aggressive in pursuing NO_x controls to address the formation of secondary particulate matter. The Bay Area Air Quality Management District has also adopted some NO_x regulations to reduce the transport of ozone into downwind areas. Naturally, CARB's motor vehicle regulations are effective statewide. Staff revised and enhanced the material in this paragraph.

Page 1-5: section titled "Analytical strategies, findings and issues"

May need to change the title of this section. Is this the results of previous studies? Should break up and better organize this section.

Staff agrees and rewrote.

Page 1-7, first full paragraph:

The Blier and Winer 1996 study could be cited as supporting evidence for the carryover hypothesis (i.e., highest O₃ Thursday-Saturday).

Staff dropped several paragraphs in this section to keep the material more focused and succinct.

Page 1-7, 1st paragraph:

This paragraph is not clear. For example, 4th line: "...were higher for NMHC and NO_x and lower for O₃" -- higher and lower compared to what? Last sentence: "Again, the ozone control program...lowered...from 1986 levels." It lowered them again? Or is the effectiveness of the program being reemphasized?

Staff dropped several paragraphs in this section to keep the material more focused and succinct.

Section 2 Comments

General comment: All reactions should be numbered to make it easier to refer to the reactions. The paper provides a photochemistry overview in a couple of different places (Section 1 Background and again in Section 2, Hypothesis 1. There should be a single, comprehensive discussion of chemistry, including a listing of the key reactions with the reactions numbered. It might be best to locate this in Section 1 background, and the discussion of the hypotheses can then refer back to this section.

Staff included a chemistry chapter in the revised report. The equations are numbered to facilitate the discussions and the identification of specific reactions emphasized in the discussion of the hypotheses in later sections.

Page 2-1, 3rd paragraph.

What decisions are being referred to in this chapter? Presumably this is a decision on control strategies. Discussions of management decisions should be separated from the scientific analysis of the weekend effect. There is a risk here that management needs may affect the science evaluation, and there is a greater danger that management decisions will become inappropriately embedded within or linked to particular, narrow scientific results.

All discussion of decision making should be moved to a separate chapter where decisions and management strategies are considered in a comprehensive approach that includes multiple pollutants. The danger in this report is that the air quality management strategy is being linked too closely to the particular findings of the weekend effect study.

Professor Tonnesen raises very valid points here about the dangers of linking air quality management decisions too closely with the scientific observations and conclusions associated with the weekend effect. Air quality management decisions, and especially those involving such a multi-faceted pollutant such as NO_x, need to be made in a larger context than just the O₃ weekend effect.

Page 2-2, H#1 Synopsis, first paragraph:

Delete the quotes on "disbenefit" and "VOC limited" These terms should already be defined in the background section. It is okay to define them again here if necessary, but the meaning of the quotes is ambiguous. This paragraph contains an important statement on the effects of NO₂ scavenging of radicals -- this should also be treated in much more detail in the background section.

Staff has done.

Page 2-2, H#1 Synopsis, second paragraph:

Second sentence "...[weekend O₃ formation]...might no longer be VOC-limited." Weekend O₃ formation might still be VOC limited but just less VOC limited relative to weekdays.

Last sentence: "If no longer precursor limited..." This is confusing - both NO_x and VOC are precursors, which is being referred to here?

Staff agrees on both counts and rewrote for more clarity. In essence, staff was discussing the O₃ formation regime where both precursors are effective in influencing peak O₃ concentrations rather than only one of the precursors (i.e., VOC-limited or NO_x-limited).

Page 2-2, H#1 Theory

The theory section (and the background section) should also explain that VOC sensitive

conditions are limited by the source of free radicals. There is always excess CO, CH₄ and slowly reacting VOC in ambient air that can react with NO_x to form O₃ if there are sufficient radical sources. The reason that these species do not react to produce O₃ at low VOC/NO_x ratios is because:

- A. NO titrates O₃ removing an important radical source, and
- B. NO₂ scavenges OH radicals.

Moreover, formation of O₃ can be VOC sensitive at relatively higher VOC/NO_x ratios if light is reduced because photolysis reactions are the primary sources of free radicals. Thus, including a description of the radical limited regime will be useful for explaining the "light-limited" soot hypothesis later in the report.

Staff has enhanced the discussion in a new section focusing on chemistry.

Page 2-3. First paragraph:

The EKMA diagram in Figure 2-1 does not extend far enough into the radical limited/VOC sensitive regime. A new EKMA diagram should be prepared specifically for SoCAB that includes lower VOC/NO_x ratios. Also, the plot should be enlarged so that illustrative arrows can be drawn to represent combinations of VOC and NO_x reductions that can result in O₃ increases.

A good suggestion that staff attempted to incorporate.

Page 2-3. 2nd paragraph:

Regarding the shape of the EKMA diagram, this section should reference the Tonnesen and Jeffries (1994) paper on NO_x inhibition of O₃ formation, and the Tonnesen and Dennis (2000a) paper that describes the effect of propagation and termination reactions on OH chain length and O₃ production. For completeness, as described in Tonnesen and Jeffries (1994) there are two major factors by which NO_x inhibits O₃ formation:

1. NO reacts with O₃ and thereby reduces O₃ photolysis as a source of O¹D
2. NO₂ reacts with OH.

The NO₂ scavenging of OH is the dominant effect but both reactions should be described for completeness.

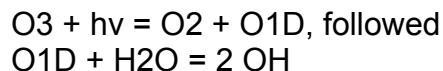
Staff has incorporated in the enhanced chemistry section.

Page 2-3. First paragraph:

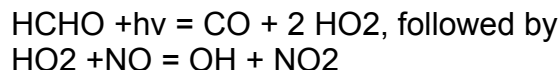
This radical production reaction sequence is incomplete – while the NO₂ photolysis reaction:



does produce an atomic oxygen free radical but this is a low energy O³P and is of minor importance in the photochemical reaction of VOC and NO_x to produce O₃. The dominant radical formation sequences are:

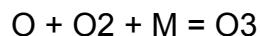


and photolysis reaction of carbonyls, especially formaldehyde (HCHO):

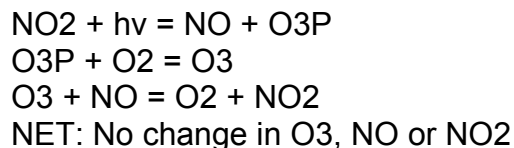


and other minor photolysis reactions, e.g. HONO, H₂O₂, and decomposition of unstable products including PAN and decay products of aromatics etc.

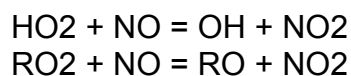
Page 2-3. Middle section list the O₃ formation reaction as:



This is an incomplete description of O₃ formation because this reaction participates in the Chapman cycle that does not promote net production of O₃:



The paper correctly states in the next paragraph that organic peroxy radicals (RO₂) cause a net change in O₃, however both hydroperoxy (HO₂) and RO₂ should be listed:



and it would be helpful to state that these reactions cause a shift in the photostationary state of the Chapman cycle that results in some net formation of O₃. All of this chemistry would best be summarized in the background section.

Expanded chemistry is provided in a new section that serves as a reference point for the discussion of the WE effect hypotheses.

Page 2-3, Next to last paragraph, beginning "Thus, in a given air parcel..."

This paragraph should also reference Tonnesen and Dennis (2000a) which provides a detailed description of the competition between VOC and NO₂ for OH radicals and suggests that the OH rate constant weighted ratios of VOC and NO_x are more useful

than VOC/NO_x as a measure of the conditions under which NO₂ inhibits or promotes O₃ formation.

Staff has done.

Page 2-4, first paragraph, first sentence:

For hypothesis one, it is required that the conditions are VOC limited on the weekdays, but they may or may not be VOC limited on the weekend. That is, higher weekend ratios cause the weekend conditions to be less VOC limited and may in fact transition to the "O₃ ridgeline" condition or even to slightly NO_x limited conditions. So, I suggest deleting the "and weekends" from the first sentence.

Staff has done.

Page 2-4, first paragraph, last sentence: "...as implied by Figure 2.1"

It would be useful to have an arrow on Figure 2.1 showing the movement from a point A to point B on the EKMA diagram. This would require a full size plot, and the EKMA surface would need to extend to higher NO_x concentrations to encompass more of the VOC limited region.

Staff attempted. Most EKMA diagrams that have been generated are based on applications and assumptions that tend to over-emphasize the NO_x disbenefit (i.e., the O₃ isopleths are more horizontal than vertical when carryover, fresh emissions, and complete chemistry are not included).

Page 2-4, Hypothetical Explanations, first bullet:

Strike "and weekend" (see comment above). Also, "eight" should include units "eight ppmC/ppm. It is not clear here at what time of the day the ratio should be less than 8 ppmC/ppm. Is it early morning or all day? The ratio will change during the day as the NO_x becomes relatively depleted compared to VOC.

Staff has done and clarified.

Page 2-4, Hypothetical Explanations, first bullet "the VOC/NO_x ratio should be higher..":

It is possible the reactivity of the VOC could differ on the weekend, so it might be better to state that the "reactivity weighted VOC/NO_x ratio should be higher..."

Staff has done.

Page 2-4, Hypothetical Explanations, fourth bullet: "NO₂ to NO ratio should be higher.."

This is a very important point. It would be useful to also mention other indicator ratios here, for example, the ratio of O₃/NO_x, HCHO/NO_x and the extent parameter.

Staff has done.

Page 2-5, Hypothesis #2: NO_x timing, first paragraph:

The first paragraph on page 2-5 states this hypothesis accurately. But let me attempt to restate it for more clarity:

At low VOC/NO_x ratios there is a low O₃ production efficiency per NO_x, and this condition typically occurs during weekday rush hours. On weekends if NO_x emissions are distributed more evenly throughout the day, the VOC/NO_x ratio will be higher and the production efficiency per NO_x will be higher, so more O₃ can be performed for a smaller amount of NO_x emissions.

Staff has clarified.

Page 2-5, Hypothesis #2: NO_x timing, second paragraph:

It is not clear what a "more active" system means, and it probably confuses the explanation here. It is possible to have a very active system with high O₃ production rates but relatively low O₃ production efficiencies per NO_x. The crux of this hypothesis is that O₃ production is more efficient per NO_x, and it should be explained in terms of NO_x being redistributed on the weekend such that relatively high VOC/NO_x ratios and high O₃ production efficiencies per NO_x are realized on the weekend compared to weekdays.

Staff has clarified.

Page 2-5, Hypothesis #2: NO_x timing, third paragraph:

Second sentence, "11 PM" should be "11 AM".

Staff has done.

Page 2-5, Hypothesis #2: NO_x timing, fourth paragraph:

The fourth paragraph makes the key point regarding this hypothesis, but it needs more elaboration, especially with respect to the policy implications in the last sentence:

The consequence of hypothesis #1 is that a weekday NO_x reduction could cause an O₃ increase. The consequence for hypothesis #2 is that a weekday NO_x reduction would cause an O₃ decrease. These two hypotheses have exactly opposite implications for the O₃ sensitivity to changes in NO_x emissions. However – as described above in the general comment section, it is premature to associate policy implications with either hypothesis. A finding that hypothesis 1 is correct would not necessarily imply that “NO_x controls are counter productive”, rather, it could just as well imply that we need even bigger and more rapid NO_x controls.

I am concerned that policy is being too closely linked to a particular science finding. The document should be careful to set out all of the issues that affect the policy decision and not implicitly link a particular policy decision to specific findings about O₃ sensitivity to NO_x.

Staff concurs in principle but the fact remains that the Board directive for this study and report was to investigate the ozone weekend effect and its implications for adopting NO_x controls. The Board desires to make the best possible decisions for protecting public health and welfare and those decisions must be based on the best available science. Thus, these scientific findings regarding the ozone weekend effect do have policy implications. However, the Board sets policy based on the full suite of environmental, social, and economic impacts associated with controlling a particular pollutant to attain health-based air quality standards.

Page 2-5, Hypothesis #2: NO_x timing, fifth paragraph:

Figure 2-2 does not convey any information about O₃ production efficiency per NO_x. It would be very helpful to add a second time-series to Figure 2-2 that represents both increments of NO_x emissions being added at 6 AM. Compared to the current plot, the new time-series would show O₃ increasing more slowly in the morning, being higher at 10 AM, but leveling off at a lower O₃ level earlier in the day. Both lines must ultimately level off in the NO_x limited regime for this hypothesis. It would be even more helpful to present in the plot the average O₃ production efficiency per NO_x for each line.

Staff considered enhancing the figure; however, there was concern about increasing the detail and complexity in the Staff Report. The main impression staff wished to convey here is that ozone formation at midday may be more sensitive to NO_x, whether from a mass standpoint or an efficiency standpoint, on weekends than on weekdays.

Page 2-5, Hypothesis #2: NO_x timing, sixth paragraph:

This paragraph uses Johnson's “light limited” terminology. This is similar to being radical limited because light is the source of the photolysis reactions. However, radical limited more accurately describes the fundamental mechanism (e.g., if we had added more HCHO, the system would no longer be “light-limited”). Since the “radical limited” concept was already introduced in the chemistry section, I strongly suggest using this terminology consistently throughout the document. It helps provide a constant theoretical vantage point and poses less risk of confusing non-scientists about the difference between “light limited” versus “radical limited” versus “VOC limited”.

Staff agrees that multiple terms are confusing and will change “light-limited” to “radical-limited”. However, because “VOC-limited” terminology is so widely used in the literature despite its subjectivity to reactivity, it will be difficult to completely eliminate its usage in the report.

Page 2-6, first full paragraph:

Along with the Lu and Chang reference, I suggest including Tonnesen and Dennis (2000a) which described in comprehensive detail the transition from VOC limited to NO_x limited conditions during the day, and also includes time-series of indicator ratios that mark this transition.

Staff has done.

Page 2-6, second paragraph:

Similar to my comment on a “more active” system, the concept of “a more primed” system is confusing. This description could equally well apply to hypothesis number 1, that is, the system is more primed because it is not inhibited by high NO_x. It should be clear that this hypothesis # 2 requires that the peak O₃ be NO_x limited on both weekends and weekdays, and that the weekend has higher peak O₃ simply because the O₃ production per NO_x was more efficient due to the way the NO_x was distributed during the day.

Staff edited the report to be more precise and specific in its discussions. Staff does not agree that the NO_x timing hypothesis requires peak O₃ formation to be NO_x-limited on both weekdays and weekends. Rather, the hypothesis only requires that the ozone be NO_x-limited on the weekend, i.e., the comparable midday activity and emissions on the WE compared to WD but it a more efficient O₃ production regime per NO_x molecule (because photochemistry has proceeded further due to less NO_x in the morning and the approximately 1 hour headstart).

Page 2-6, third paragraph: “...because the advanced photochemistry has driven the [weekend] system to the NO_x limited regime.”

See my comment on the previous paragraph – this hypothesis requires that peak O₃ must be NO_x limited on both weekdays and weekends. If the cause of the weekend effect is that weekday O₃ was inhibited by high NO_x, we essentially have reduced this to hypothesis number 1.

Staff does not believe the WE effect hypotheses are independent or mutually exclusive and, in fact, likely work together to various degrees to create and enhance the effect. Although photochemical reactions remain the same on WD and WE, the emissions have a different mix, distribution, and timing on WE than on WD. This creates a different environment in which the photochemistry operates. In particular, the atmosphere, especially aloft (above the surface layer with fresh emissions), has moved more rapidly from a radical-limited ozone forming regime to a

NO_x-limited regime by midday on the WE when VOC and NO_x emissions are comparable in magnitude to WD emissions. With no shortage of radicals and photolysis at its peak, the fresh NO_x emissions are rapidly oxidized and photolyzed, continuing the enhancement of ozone concentrations.

Page 2-6, fourth paragraph: "...active (efficient)..."

"Active" and "efficient" do not have the same meaning. Active is the rate or amount of O₃ production (P(O₃)). Efficiency should be defined as the number of O₃ produced per NO_x consumed (P(O₃)/P(NO_x)). It is possible to have high P(O₃) at relatively low P(O₃)/P(NO_x) if we have very high concentrations of VOC and NO_x.

The terminology has been modified to be more precise and yet understandable to non-chemists.

Page 2-7, hypothetical expectations:

Another expectation should be added: the reactivity weighted ratio of VOC/NO_x should be "flatter" on the weekend compared to the weekday. That is, VOC/NO_x should be higher on the weekend morning but lower later in the day. The same is true of the other indicator ratios. This hypothesis requires that the weekday "burn up" its NO_x emissions at times of low P(O₃)/P(NO_x) and therefore the weekday must become NO_x limited earlier in the day. The modifications I suggested to Figure 2-2 would illustrate this nicely.

Staff had not thought of the hypothesis from this perspective. Staff hypothesized that the greater reduction in NO_x emissions than VOC emissions on weekend mornings allowed the O₃ photochemistry to move toward the peak O₃ production ridgeline sooner than on weekdays. With the atmosphere closer to its peak O₃ formation potential on the WE compared to the WD, the comparable precursor emissions from motor vehicles at midday on WE and WD enable O₃ formation to continue its rapid growth at midday on the WE. Professor Tonnesen's perspective of the hypothesis is consistent with the relative WD versus WE difference in diesel vehicle activity and its potential influence on O₃ concentrations.

Page 2-8, Carry over hypothesis: "as shown in"

There appear to be extra carriage returns before "Figure 2-3".

Staff has deleted CR.

Page 2-9, first paragraph

PAN is a likely culprit in the carry over hypothesis, so you might change "(e.g. HONO)" to "(e.g. HONO and PAN)".

Staff has done.

Page 2-9, second paragraph

This paragraph suggests that the carry over effect is related to lower NO_x emissions and less quenching of radicals – this is an identical restatement of hypothesis number one. The carry over effect must be due entirely to more O₃, PAN, HONO and other precursors being carried over aloft.

Hypothesis #1 entails more than just O₃ quenching. To separate the effect of O₃ quenching from the NO_x-disbenefit chemical regime, staff will incorporate a seventh hypothesis into the report. Once again, the multiple processes are complex and the hypotheses are not necessarily independent and exclusive of each other. It is likely that the process that is the focus of each hypothesis contributes to one degree or another to the WE effect. The Carryover Hypothesis focuses on the interaction of the air aloft (and the O₃ generated therein) with the fresh emissions in the surface layer where ambient measurements are made. This hypothesis also includes the premise that ambient measurements near ground level do not characterize the thicker layer of ozone formation several hundreds of meters above the lowest hundred or two meters of air near the emission sources. If the air aloft were comparable to what is observed in the lowest layer, then Monday with its prodigious fresh emissions and the carryover of O₃ from the day of the week with the highest concentrations (i.e., Sunday), then Monday should have the highest O₃ concentrations of the week. Instead, Monday generally has the lowest O₃ concentrations of any day of the week.

Page 2-10, third, fourth and fifth paragraphs:

This discussion describes the carry over effect as being a combination of hypotheses numbers 1 and 2. While it is possible and even likely that all three do play a role, they should not be combined as a single explanation here under hypotheses number 3.

This hypothesis requires that more odd O₃, NO₂, HONO and PAN be carried over aloft on weekends. If it is stated such that more radicals are carried over the implication is that the weekday was radical limited (i.e., hypothesis number 1).

It is difficult to isolate all the interacting factors and processes in the analysis of ambient data. Staff attempted to better isolate the hypothesis in each discussion

Page 2-10: hypothetical expectations

All of the hypotheses in this section should be deleted except for the following:

- ✓ Large reservoirs of ozone and precursors aloft should be the norm rather than the exception.
- ✓ Carryover of O₃ and precursors should be largest on the Friday and Saturday night.

Staff rewrote to better articulate the hypothetical observations and the description of the hypothesis.

Page 2-12, Hypothesis # 6.

The implication of this hypothesis is that O₃ formation is radical limited on weekdays, and that greater radical production (from increased actinic flux) enhances O₃ production on weekends. This hypothesis is consistent with hypothesis one which also requires that O₃ formation be radical limited on weekdays. This hypothesis mean that some of the weekend O₃ effect should be attributed to the change in actinic flux and that some would be attributed to reduced weekend NO_x.

True. If the hypothetical relationships are borne out under further study, these two hypotheses taken together would provide additional circumstantial evidence toward the potentially significant role of diesel emission sources.

Page 3-6, Finding #8:

This finding states that the “pattern is consistent with lower and less reactive VOC emissions with little change in VOC/NO_x ratio”. The discussion on this finding should distinguish between “lower” versus “less reactive” VOC. These will have different implications for possible changes in NO_x emissions at a constant VOC/NO_x ratio. O₃ should peak later in the day for less reactive VOC at a constant VOC/NO_x ratio, however, for lower VOC at a constant VOC/NO_x ratio this may not be true.

Staff deleted “lower”.

Page 3-7, Finding #11:

Need to clarify the meaning of “more active” in this finding. In the discussion here it appears to mean that a larger fraction of the NO_x was oxidized to inert NO_z. However it could mean that P(O₃) was higher or P(O₃)/P(NO_z) was higher.

Staff has clarified.

Page 3-8, Finding #8:

“...between 4.0 and 9.0.” Should give units ppmC/ppm when ever values of VOC/NO_x are discussed. Also, it would be useful to describe the time of day at which they measurements are made – is there data on how the VOC/NO_x ratio varies during the day? Time-series of this ratio would be very useful for testing the time shifting hypothesis.

Staff has provided more detail and clarification.

Page 3-6, Finding #13:

The definition of "Reactivity" needs to be defined. Here it appears to be VOC reactivity is in "incremental reactivity" scales. At other places in the report "reactivity" appears to mean the amount or rate of O₃ production.

Staff has clarified the discussion.

Page 3-8, Finding #13, first bullet:

This finding requires some clarification. Regarding the conclusion "the effect of carryover would be greater on weekends compared to weekdays": As described here the implication is that carry over is more important relative to emissions on weekends compared to weekdays. However, we are really concerned with whether carryover is larger in an absolute sense on weekends than week days, i.e., the amount of O₃ and precursors carried over. It is hypothetically possible that carry over could be smaller on weekends yet more important relative to the smaller weekend emissions, yet this would not produce a weekend effect.

Staff differs with Professor Tonnesen on the concept of carryover. Although the amount of carryover is a factor, the focus is on the relative impact of the O₃ formed aloft versus the O₃ formed near the ground. Furthermore, staff notes that ambient measurements at ground level do not accurately characterize the O₃ conditions aloft.

The role of carbonyls especially HCHO should be specifically addressed in carry over. If there is a greater amount of carbonyls carried over on the weekend this could explained higher O₃ production rates on weekend morning. Oxygenates are difficult to measure and there may not be good data available for this, even at the PAMS sites.

Staff elaborated further and clarified but in the Hypothesis chapter rather than the Findings chapter.

Page 4-2, Conclusion #3:

A stronger conclusion can be drawn here regarding the benefits of NO_x controls. In the first paragraph I suggest deleting the last sentence beginning: "Until the cause of the ozone weekend effect..." and replacing it with a more strongly worded conclusion at the end of this section, for example:

"Even if there is found to be a NO_x disbenefit for weekend O₃ for present day conditions, NO_x reductions remain a necessary and essential element of air quality improvement plans for several different pollutants. A finding of a NO_x disbenefit for present conditions could lead to a strategy of requiring larger reduction in NO_x emissions so that the air basin shifts to a NO_x limited regime. In this NO_x limited

condition, lower weekend NO_x emissions would then provide beneficial reduction in both O₃ and other pollutants.”

Staff emphasized the widespread and diverse impacts of NO_x emissions on people and the environment in the final version.

Page 4-2, Conclusion #6b, 4th bullet:

The weekend early afternoon NO_x is 60 to 80% of weekday NO_x. With higher weekend O₃ levels, it is possible that NO_x will be removed from the system more rapidly on weekends, so lower afternoon NO_x on weekend could also reflect a higher removal rate.

Staff has noted in revised report.

Page 5-1, Recommendation #1:

The value of a new, large scale field study should be seriously considered. The 18 month intensive field study would likely be prohibitively expensive, and a scaled back field study might not be sufficient to meet the objectives. The usefulness of data collected in previous major field studies should also be carefully reviewed. Moreover, previous tracer studies have been difficult to interpret and of questionable value.

It is likely that an enhanced long term monitoring network will be more useful than a new major field study. The enhanced long term network would include continuous monitoring of some “non-routine” measurements that can be used for assessing O₃ sensitivity to VOC and NO_x in observation based models (OBMs). Species should include HCHO, true NO₂, total NO_y, aerosol nitrate and speciated VOC. Sites should include the gradient in VOC/NO_x condition from urban Los Angeles to downwind sites including Riverside and the Palm Desert areas to capture the transition from VOC sensitive to NO_x sensitive chemistry. Enhanced sites should also be included in the Bay Area and central valley air basins. The existing PAMS network should be reviewed with respect to its adequacy for representing location with and without weekend effects. The complement of measurements in existing PAMS sites should also be reviewed to determine the adequacy for calculation of observation based methods that characterize VOC sensitive and NO_x sensitive O₃ regimes.

The advantage of enhanced long term monitoring sites is that they will provide a sufficient number of days to calculate statistically significant differences in weekends versus week days. An enhanced network will also aid in monitoring the long term trends in precursors and O₃ and in the sensitivity of O₃ to VOC and NO_x. Finally, an enhanced long term monitoring network will be more useful for developing accurate models of air quality and for tracking progress toward attainment of air quality standards.

Staff concurs that any field study would need to be well-designed and monitor continuously and not in an episodic nature. Given the current fiscal crisis in the State of California, it is unlikely

that the routine monitoring network could be enhanced. In fact, it is likely the existing network would be scaled back in number and comprehensiveness (full suite of routine or enhanced measurements).

Page 5-5, Recommendation #4:

New laboratory studies should be a high priority. For the 3 bullets listed on page 5-5, the third “carry-over” aloft can be deleted because this can not be evaluated in lab studies. However, two new bullet should be added:

- Laboratory studies of potential indicators and observation based methods for characterizing conditions in which O₃ is primarily sensitive to VOC or to NO_x. This is one of the most promising approaches for understanding the weekend effect, yet there has been no laboratory evaluation of indicators or OBMs.
- Evaluation of sources and sinks of free radicals (OH, HO₂, RO₂). The budgets of these species are critical for correct representation of both the production rate of O₃ and the sensitivity of O₃ to VOC and NO_x. There remain large uncertainties in the budgets of these species (e.g., Tonnesen, 1999). They have not been measured in any of the chamber experiment that were used to develop our current photochemical mechanisms.

Staff has done.

References

Tonnesen, G. S. and R. L. Dennis, (2000a) Analysis of radical propagation efficiency to assess ozone sensitivity to hydrocarbons and NO_x. Part 1: Local indicators of odd oxygen production sensitivity, *J. Geophys. Res.*, **105**, 9213–9225.

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